Determination of Nitrogen in Nitro and Oxime Compounds by the Iodic Acid Decomposition Method

By Shigeru OHASHI

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In the previous investigation[1] on the determination of nitrogen in organic compounds by the iodic acid decomposition method the author has found that for analyses of ammonium salts, amines, azo-compounds, pyrroles, thiazoles, etc., satisfactory results are obtained by means of this new method, but nitro and oxime compounds, etc. do not give good results.

The outline of this method is as follows. An organic compound containing nitrogen is decomposed by heating with a potassium iodate-strong phosphoric acid mixture in a special reaction vessel. By sending the liberated nitrogen with carbon dioxide into an azotometer, which is filled with potassium hydroxide solution, the nitrogen can be determined gas-volumetrically. The reason why the nitrogen in nitro and oxime compounds can not be directly estimated by this method may be due to the fact that the nitrogen in these compounds is already in an oxidized state and is liberated by the iodic acid decomposition, at least partially, merely as nitrogen monoxide, or dioxide, which is absorbed in potassium hydroxide solution in the azotometer.

The purpose of the present investigation is to extend this method to the determination of nitrogen in nitro and oxime compounds. It has previously been shown that the nitrogen in amine compounds can be easily determined by this method. Therefore, if the nitrogen of a nitro or oxime form could be reduced to an amine form by a somewhat simple treatment, it may be possible to determine the nitrogen in nitro or oxime compounds by the reduction and the subsequent iodic acid decomposition.

For this reason, the present study was mainly aimed at finding out the most suitable reducing agent against these compounds. From the results of the experiments described later, it was concluded that iron metal with diluted sulfuric acid is the best reducing agent for the present purpose.

In this paper the discussion of the reducing agents, the recommended procedure of this method, and the analytical results of several nitro and oxime compounds are described.

In the author's laboratory strong phosphoric acid has been used not only for the determination of nitrogen in organic compounds, but also for the determination[2] of the oxidation value of organic compounds and the determination[3] of elementary carbon such as active carbon and graphite. Since hitherto the property of strong phosphoric acid has not been stated in these papers, the specific gravity and the chemical composition of strong phosphoric acid used in these studies are also described complementally.

Reducing Agents

The reducing agent used in this method must have the following properties: A nitro or oxime radical is quantitatively reduced by it to an amino radical; the reduction should be done at temperatures lower than 100°C, because many nitro and oxime compounds are easily volatilized at higher temperatures; and after the reduction the remaining reducing agent does not interfere with the subsequent decomposition procedure of the reduced product and the estimation of nitrogen.

Since the decomposition process is carried out in a strong phosphoric acid medium, it seems to be convenient for the reduction process also to be done in the same medium. Therefore, at first, zinc metal in strong phosphoric acid was used as a reducing agent. But, using this agent, the analyses for *p*-nitroacetanilide and *α*-dinitrophenol gave low results. Probably it may be due to the fact that zinc metal does not easily dissolve in strong phosphoric acid at a relatively low temperature.

Next, tin(II)-strong phosphoric acid was tested, because it was found in the anthor's laboratory that this agent can reduce sulfates[4] or various organic sulfurs[5] to hydrogen sulfide. But it was

1) S. Ohashi, This Bulletin, 28, 177 (1955).

2) S. Ohashi, This Bulletin, 28, 171 (1955).

3) T. Kiba, S. Ohashi, T. Takagi and Y. Hirose, *Japan Analyst*, 2, 446 (1953).

4) T. Kiba, T. Takagi, and Y. Yoshimura, Presented at the Symposium of Analytical Chemistry at Kinki University, October 30, 1954.

5) S. Ohashi, I. Kishi, Presented at the same Symposium described above.

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not favorable, as it produces, when heated, a certain gas, probably hydrogen, which can not be absorbed in potassium hydroxide solution in the azotometer.

Glucose was used by J. Noguchi[6] as a buffer agent in the micro-Dumas method for the analyses of nitro compounds. Accordingly as an example α-dinitrophenol was decomposed with iodic acid-strong phosphoric acid in the presence of glucose, but the test also failed, because too much iodine was liberated by the oxidation of glucose and the sample.

Hypophosphorous acid in strong phosphoric acid was not suitable for the present purpose, since it liberates, when heated, phosphine, which can not be absorbed in alkali solution in the azotometer.

In view of the above facts the reduction methods using strong phosphoric acid were given up. Then the reduction in diluted mineral acids was investigated.

Iron metal powder in hydrochloric acid was tested, since it has been commonly used to reduce nitro compounds. The results for picric acid gave values which were almost correct. But it was not favorable, because the liberated chlorine reacts with iodine and mercury in the azotometer to produce iodine chloride and mercuric chloride, which block the capillary of the azotometer.

Finally it was found that iron metal powder in diluted sulfuric acid does not possess the various defects described above and is the most suitable reducing agent.

Apparatus and Reagents

The same apparatus described in the previous paper[7] was used. Only the reaction vessel is illustrated in Fig. 1.

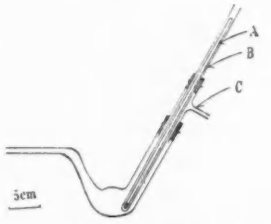

Fig. 1. Reaction vessel
A: Thermometer
B: Thermometer-protecting Tube
C: Gas-introducing Tube

The following reagents were the same ones that were used in the foregoing paper[8]; strong phosphoric acid, potassium iodate, carbon dioxide, and potassium hydroxide solution. Acetone, 6 N sulfuric acid, and iron metal powder were all of extra pure grade.

Procedure

Weigh accurately a 10 to 30 mg. sample, depending upon its nitrogen content, into a small weighing tube; choose the sample weight so that the volume of the nitrogen formed will be 1 to 5 ml. Place the weighing tube containing the sample in the reaction vessel, add 1 to 1.5 ml. of acetone, and dissolve the sample in it. Next, add 50 to 60 mg. of iron metal powder and 1 ml. of 6 N sulfuric acid. Gently heat the mixture on a water bath. By this treatment the nitro or oxime compound is reduced to the corresponding amine compound and at the same time the excess of iron is dissolved in sulfuric acid. Continue heating on the water bath until all the acetone and the greater part of the water are expelled. At the end of this time the dissolution of the iron is almost always complete.

After cooling the contents of the vessel, add 3 to 5 ml. of strong phosphoric acid and two or three times as much of the theoretically required amount of potassium iodate in it.

Now insert a gas-introducing tube, a thermometer, and a thermometer-protecting tube into the reaction vessel, and connect the vessel with a carbon dioxide generator and a calcium carbonate-filled guard tube. After removing the air present in the reaction vessel, connect it to an azotometer.

Heat the mixture in the vessel on a small electric heater at 200°C to 250°C. After the complete decomposition of the sample, transfer the gas in the vessel into the azotometer and carbon dioxide is then allowed to be introduced. Read the volume of the nitrogen, the room temperature, and the atmospheric pressure at this time and calculate the percentage of the nitrogen by using these values.

Results of Analyses and Discussion

Analyses of various known nitro and oxime compounds were carried out by this method. These results are summarized in Table I. As shown in Table I analyses for *p*-nitrophenol, α-dinitrophenol, picric acid, *p*-nitroacetanilide, sodium hexanitrodiphenylamine, *m*-nitro-*o*-anisidine, dimethylglyoxime, cyclohexanone oxime, and α-oxime of phenylpropionic acid gave satisfactory results. In the case of *p*-nitroacetanilide, sodium hexanitrodiphenylamine, and *m*-nitro-*o*-anisidine, the total nitrogen contents of both the nitro and amino radicals were determined.

The accuracy of the results obtained is within ±2%. The time required for an analysis is fifty minutes.

It is necessary for a rapid and complete reaction between a sample and a reducing agent that the sample be homogeneously dissolved in acetone.

If the quantity of sulfuric acid to be added is deficient, the reduction can not be carried out completely and if it is in too excess, after the reduction, strong phosphoric acid is so much diluted that the sample can not be decomposed perfectly.

6) J. Noguchi, Scientific Papers from the Osaka University, No. 22, February 1951.
7), 8) S. Ohashi, This Bulletin, 28, 177 (1955).

TABLE I

DETERMINATION OF NITROGEN IN VARIOUS NITRO AND OXIME COMPOUNDS

Substance	Nitrogen Content %	Sample Weight mg.	Nitrogen Content Found %	Nitrogen Content Deviation %
p-Nitrophenol $C_6H_4(OH)NO_2$	10.01	13.1	9.99	−0.02
		13.7	9.98	−0.03
		11.1	10.09	+0.08
		14.5	10.07	+0.06
		10.8	10.02	+0.01
		10.9	10.11	+0.10
α-Dinitrophenol $C_6H_3(OH)(NO_2)_2$	15.19	14.9	15.39	+0.11
		13.3	15.33	+0.14
		12.9	15.15	−0.04
		11.1	15.23	+0.04
		11.5	15.20	+0.01
		13.9	15.20	+0.01
		13.0	15.11	−0.05
Picric acid $C_6H_2(OH)(NO_2)_3$	18.34	7.8	18.30	−0.04
		11.4	18.32	−0.02
		10.3	18.49	+0.15
		11.0	18.35	+0.02
		7.7	18.24	−0.13
		9.1	18.01	−0.36
p-Nitroacetanilide $C_6H_4(NO_2)NHCOCH_3$	15.55	13.3	15.55	0.00
		15.7	15.58	+0.03
		14.6	15.64	+0.08
		15.0	15.69	+0.14
		14.3	15.69	+0.14
		13.9	15.74	+0.19
Sodium hexanitrodiphenylamine $NaN(C_6H_2(NO_2)_3)_2$	21.26	10.5	21.21	−0.05
		11.4	20.95	−0.31
		12.4	21.25	−0.01
		10.1	21.14	−0.12
		10.9	21.27	+0.01
		11.1	21.07	−0.19
m-Nitro-*o*-anisidine $C_6H_3(NO_2)(NH_2)(NH_2)OCH_3$	16.66	11.4	16.58	−0.08
		8.1	16.66	0.00
		14.8	16.60	−0.06
		16.7	16.45	−0.21
		11.2	16.62	−0.04
Dimethylglyoxime $HON(CH_3)C{\cdot}C(CH_3)NOH$	24.13	12.6	24.15	+0.02
		12.1	24.20	+0.07
		23.3	24.08	−0.05
		16.7	24.22	+0.09
		16.4	24.04	−0.09
		20.4	24.14	+0.01
Cyclohexanone oxime $C_6H_{10}NOH$	12.38	24.7	12.37	−0.01
		28.0	12.27	−0.11
		24.6	12.32	−0.05
		26.5	12.36	−0.02
		24.3	12.40	+0.02
		24.0	12.40	+0.02
α-Oxime of phenylpropionic acid $C_6H_5CH_2C(NOH)COOH$	7.82	26.4	7.67	−0.15
		28.6	7.85	+0.03
		22.6	7.66	−0.16
		23.9	7.86	+0.04
		26.1	7.97	+0.15
		28.4	7.77	−0.05
		28.6	7.79	−0.03

On many occasions excess iron metal powder is all dissolved in sulfuric acid by means of the above mentioned procedure. If it remains, the hydrogen formed by the reaction between iron and strong phosphoric acid may be transferred with nitrogen to the azotometer and gives a serious error. Therefore, in such a case, before the addition of potassium iodate the remaining iron powder should be dissolved by heating with strong phosphoric acid.

Strong Phosphoric Acid

The strong phosphoric acid used in the experiments below was prepared from common 89% orthophosphoric acid by using an apparatus shown in Fig. 2. About 18 g. of the orthophosphoric acid was dehydrated by heating until the temperature of the liquid attained various points, ranging from 200° to 320°C at intervals of about 20°C.

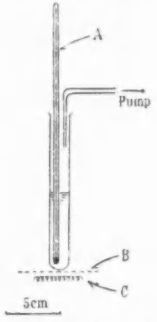

Fig. 2. Dehydration Apparatus
A: Thermometer
B: Wire Gauze
C: Electric Heater

The specific gravity of the strong phosphoric acid obtained in this manner at 15°C was estimated by means of a specific gravity bottle.

Since some phosphoric acid is expelled with water during the dehydration, a percentage of phosphorus pentoxide in the prepared strong phosphoric acid can not be calculated from the decrease of the total weight of the sample. As pyro- or triphosphoric acid is not completely converted into orthophosphoric acid even by heating with water for thirty minutes, it is undesirable to use a direct titrimetric method with a standard sodium hydroxide solution for the determination of the total phosphorus pentoxide. Therefore it was determined gravimetrically as magnesium pyrophosphate.

From the obtained percentage of phosphorus pentoxide and the diagram reported by R. N. Bell[9], which shows the relation between the content of phosphorus pentoxide and the chemical composition of strong phosphoric acid, the content of ortho-, pyro-, and triphosphoric acid in the sample can be estimated respectively.

All of the above-mentioned results are shown in Table II. According to R. N. Bell strong phosphoric acid is defined as phosphoric acid containing more than 72.4% phosphorus pentoxide, which corresponds to the phosphorus pentoxide content of 100% orthophosphoric acid. According to this definition, in Table II, only the acids having a specific gravity higher than 1.882 are the true strong phosphoric acid.

If the dehydration condition changes, a different strong phosphoric acid is formed, even though heated to the same temperature. For example, when 400 g. of 89% orthophosphoric acid is dehydrated until its temperature reaches 300°C, the resulting strong phosphoric acid has a specific gravity of 1.932, which is greater than that obtained in the above-mentioned experiments. This is probably due to the fact that, when the larger amount of the acid is used, the dehydration takes place more effectively than in the case of the smaller amount. The so-called "300°C strong phosphoric acid" used in the author's laboratory has a specific gravity of about 1.93.

Summary

(1) The iodic acid decomposition method for the determination of nitrogen in organic compounds, which has been reported already by the author, was extended to analyses of nitro and oxime compounds.

9) R.N. Bell, *Ind. Eng. Chem.*, **40**, 1464 (1948). L.F. Audrieah, "Inorganic Syntheses, Volume III", McGraw-Hill Book Company, Inc., New York, (1950). p. 89.

TABLE II

SPECIFIC GRAVITY AND CHEMICAL COMPOSITION OF VARIOUS STRONG PHOSPHORIC ACIDS

Dehydration Temp. °C	Initial Weight g.	Final Weight g.	Remains Weight %	Specific Gravity at 15°C	P_2O_5 %	H_3PO_4 %	$H_4P_2O_7$ %	$H_5P_3O_{10}$ %
202	17.574	16.570	94.28	1.805	69.23	95.6	—	—
218	17.684	16.276	92.04	1.833	70.52	97.4	—	—
241	17.657	15.971	90.46	1.865	72.21	95	1	4
259	17.910	15.969	89.18	1.882	72.97	90	5	5
281	17.974	15.767	87.72	1.909	74.15	82	12	6
300	17.315	15.022	86.78	1.925	74.63	76	18	6
320	17.873	15.274	85.51	1.948	75.75	65	28	7
300	400	—	—	1.932	—	—	—	—

(2) In a reaction vessel, a samplew as dissolved in acetone, reduced with a reducing agent to the corresponding amine, and then decomposed by heating with a mixture of iodic acid and strong phosphoric acid. The liberated nitrogen was determined by means of an azotometer.

(3) After testing many reducing agents it was concluded that a mixture of iron metal powder and diluted sulfuric acid was the best.

(4) For various nitro and oxime compounds satisfactory results were obtained by means of this modified method.

(5) The specific gravity and the chemical composition of strong phosphoric acid prepared in the various conditions have been described complementally.

The author wishes to thank Prof. T. Kiba for his encouragement and valuable advice during the course of this investigation, Prof. J. Noguchi and Prof. Y. Kurata for supplying some of the samples used in this study, and Mr. T. Takagi and Mr. Y. Sasaki for their helpful assistance. The cost of this research has been partly defrayed from the Scientific Research Grant from the Ministry of Education.

Department of Chemistry,
Faculty of Science,
Kanazawa University,
Kanazawa

Lower Members of Diethoxycyclopolysiloxanes from Diethoxydichlorosilane

By Rokuro ŌKAWARA, Saburo HOTTA and Toshiro SHIMURA

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Many series of synthesized compounds of linear and cyclopolysiloxanes have been described in the literature[1]. Diorganocyclopolysiloxanes, $(RR'SiO)_n$ and organohydrocyclopolysiloxanes, $(RHSiO)_n$ have been prepared by the hydrolysis of the corresponding dichlorosilanes or dialkoxysilanes. In these cyclopolysiloxanes, cyclotrimer (n=3) was found to be the first member of the series. In the mineral silicates of natural source, skeletal structure of cyclotrisiloxane was also found[2]. Among the alkoxycyclopolysiloxanes which may be considered to be similar to the mineral silicates in their structure, only a seris of dibutoxycyclopolysiloxanes[3], $((C_4H_9O)_2SiO)_n$ (n=3, 4, ...) was studied. In a series of diethoxycyclopolysiloxanes, only cyclotetramer[4], $((C_2H_5O)_2SiO)_4$ was prepared and the other members of this series have not been reported. This paper will describe the preparation and properties of the lower members of diethoxycyclopolysiloxanes (n=3, 4 and 5).

Diethoxydichlorosilane reacts vigorously with water or water vapor instantaneously and the liberated hydrogen chloride causes the fission of ethoxy group from silicon and there remain silica and ethanol as the hydrolysis products. In the previous paper[5] the hydrolysis of triethoxychlorosilane, $(C_2H_5O)_2SiCl$ against the bound water of inorganic salts such as $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ was carried out to assure whether the selective hydrolysis of Si-Cl without the fission of ethoxy group could occur or not. The result obtained showed that the selective hydrolysis occurred in part but the accompanying fission of ethoxy group could not be prevented.

In this experiment, the reaction of diethoxydichlorosilane with sodium bicarbonate, which has the ability to convert Si-Cl to Si-O-Si and the acid accepting function in a molecule, was carried out in the hope of acquiring silanediol or siloxanes by the following reaction.

$$(C_2H_5O)_2SiCl_2 + 2NaHCO_3 = (C_2H_5O)_2Si(OH)_2 + 2NaCl + 2CO_2.$$

But the result of this experiment showed that the product was mainly composed of tetraethoxysilane and a high boiling viscous liquid. This reveals that the fission of ethoxy group occurred in the course of the reaction. Then the hydrolysis was car ried out by us-

1) E. Rochow, "An Introduction to the Chemistry of the Silicones" John Wiley & Sons, New York, 1951.
2) W. L. Bragg, "Atomic Structure of Minerals" London, 1937.
3) R.K. Iler, *Ind. Eng. Chem.*, **39**, 1384 (1947).
4) T. Takatani, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **72**, 765 (1951); **74**, 890 (1953) (in Japanese).
5) R. Ōkawara, *J. Chem. Soc. Japan. Ind. Chem, Sec.*, 55, 678 (1952) (in Japanese).

ing pyridine as an acid acceptor and the lower members of diethoxycyclopolysiloxanes could be isolated. The conditions of hydrolysis are given in Table I.

At first, the hydrolysis was carried out at the constant temperatures of 0°C, 30°C, 50°C and 70°C, respectively. On fractionation, a small amount of the cyclotrimer was found to be formed accompanying the linear trimer in limited ranges of the hydrolysis temperature, e.g., at 30°C and 50°C, while the cyclotetramer was found to appear at each hydrolysis temperature except 70°C. At 70°C, only the linear polymers could be obtained owing to the increasing fission of the ethoxy group. As it seemed very difficult to separate the cyclotrimer from the linear trimer by fractionation, the hydrolysis conditions have been pursued which liberate each one of these compounds independently. It was found that when the hydrolysis was rapidly carried out by adding chlorosilane to the ice-cooled hydrolyzing medium with vigorous stirring, good yield of the cyclotrimer could be obtained without the formation of the linear trimer. From the residue of these hydrolyzates, the cyclopentamer was also obtained. Data of these cyclocompounds are given in Table III.

The cyclotrimer reserved in a sealed glass ampulla became viscous on prolonged standing. The changes of refractive index, density and molecular weight were determined after 200 and 300 days. Trimethylcyclotrisiloxane, $(CH_3HSiO)_3$[6] has been the only example of an unstable cyclotrimer. Now, hexaethoxycyclotrisiloxane seems to be another example of the unstable cyclotrimer.

Experimental

Starting Materials.—Diethoxydichlorosilane used in our experiments was prepared by adding 2 moles of absolute ethanol to 1 mole of silicon tetrachloride with vigorous stirring. After the addition, the mixture was heated gradually to 80°C with stirring. Then the mixture, which was mainly composed of ethoxytrichlorosilane, diethoxydichlorosilane and triethoxychlorosilane was fractionated through a helices packed column of about 20 theoretical plates. The crude diethoxydichlorosilane having the boiling point 130°C to 140°C was rigorously fractionated through the same column and the middle portion of the constant boiling fraction (136°C) was taken as the starting material. Analysis for hydrolyzable chlorine by hydrolysis in water and titration of the liberated acid indicated that our sample was pure diethoxdichlorosilane.

Anal. Found: Cl, 37.2%. Calcd. for $(C_2H_5O)_2SiCl_2$: Cl, 37.5%.

6) S.D. Brewer, *J. Am. Chem. Soc.*, **70**, 3962 (1948).

Hydrolysis with Sodium Bicarbonate.—Sodium bicarbonate (25 g., 0.3 mole) was added to the mixture of diethoxydichlorosilane (19 g., 0.1 mole) and 100 cc. of benzene. The violent reaction did not occur differently from the case of partially alkolyzed alkylchlorosilanes[7]. The mixture was heated to refluxing with stirring, but the fuming chlorine compound was stil found in the benzene layer after refluxing for two to three hours and it was not easy to make a trace of the fuming compound disappear with a short time.

From the similar three runs 18 g. of the chlorine free product was obtained. On fractionation, 8 g. of tetraethoxysilane and a small amount of hexaethoxydisiloxane were found. The residue was a high viscous liquid. This reaction was not further examined, for the formation of a large amount of tetraethoxysilane in the product reveals the fission of the ethoxy group during the course of reaction.

Hydrolysis in Pyridine Solution.—(a) *Hydrolysis and fractionation of the hydrolyzate.*—As described above, the hydrolysis of diethoxydichlorosilane with sodium bicarbonate failed to obtain the lower members of cyclocompounds; the hydrolysis in a wet pyridine was therefore carried out. After several experiments the most convenient method of hydrolysis was adopted.

In a 2 *l* three-necked flask equipped with an efficient stirrer, a reflux condenser and a dropping funnel, distilled pyridine which was dehydrated on the solid sodium hydroxide, a slight excess of water required to convert $(C_2H_5O)_2SiCl_2$ to $(C_2H_5O)_2SiO$ and benzene as a diluent were placed. To this hydrolyzing mixture, diethoxydichlorosilane was added with vigorous stirring. The amount of the reagents and the conditions of hydrolysis are given in Table I. After the addition of chlorosilane, the mixture was stirred until the odor of hydrogen chloride or chlorosilane had completely disappeared from the mixture. The product was filtered from pyridine hydrochloride and thoroughly washed with ca. 500 cc. of water over five times to separate the product from pyridine hydrochloride and dehydrated on a calcinated sodium sulfate. When the pyridine hydrochloride was present in the product, it caused the product to decompose in the course of fractionation at a high temperature. After benzene and a slight excess of pyridine were distilled off, the product amounted to Pg. as is shown in Table I. The oily product was simply distilled under 10 mmHg by using a Claisen flask. Tetraethoxysilane (L_1) distilled out, then the remaining oily product was further distilled under 1 mmHg and the distillate coming out below 200°C was collected. Since in these distillations, the stil-pot temperature was not over 300°C, it may be supposed that the thermal rearrangement of polysiloxanes[8] did not occur. The total amount of the distillate obtained under 10 and 1 mmHg (T) and the remaining residue (R_1) in weight percent of P. are also given in Table I.

7) R. Okawara et al., This Bulletin, **28**, 360, 364 and 367 (1955).

8) W. Patnode and D.F. Wilcock, *J. Am. Chem. Soc.*, **68**, 358 (1946).

The distillate under 1 mmHg was rigorously fractionated through a high efficient semi-micro Stedman column of about 60 theoretical plates and the refractive index and the silicon content of the distillate were determined throughout the distillation. The amount of the succeeding plateaus including the intermittent fractions cut on the distillation curve and the silicon content of these plateaus are given in Table II.

that of cyclotetramer (C_4). In Expt. 2 and 3, the trimer fraction may be seen to be composed of cyclotrimer (C_3) and linear trimer (L_3) and the following fraction may also be seen to be composed of C_4 and a small amount of linear tetramer (L_4). From its silicon content, the trimer fraction found in Expt. 4 was L_3 and the following plateau was that of L_4. The higher the reaction temperature, the larger the amount of the fractions

TABLE I

HYDROLYSIS OF DIETHOXYDICHLOROSILANE

In each experiment, diethoxydichlorosilane (150 g., 0.8 mole) was added to the mixture of pyridine (140 g., 1.8 moles), water (15 g., 0.83 mole) and the indicated amount of benzene.

		Hydrolysis				Simple Distillation of P.	
Expt. No.	C_6H_6	Temp.	Dropping Rate of Chlorosilane	Product (P.)		~200°C/1 mm. (T)	Residue (R_1)
	g.	°C	g./min.	g.	%Theory	%P.	%P.
1	155	0	1.7	82	77	30	70
2	250	30	2.2	94	89	62	38
3	250	50	2.0	90	85	70	30
4	250	70	2.0	73	70	82	18
5	145	0–(—)	6.0	90	85	55	45
6*	250	−5–(31)**	12.0	90	85	46	54
7*	250	0–(52)	20.0	98	92	54	46
8	250	0–(54)	37.5	89	84	43	57
9*	250	0–(—)	150.0	87	83	58	42

* Diethoxydichlorosilane was cooled to 0°C before hydrolysis.

** The value in parentheses indicates the highest temperature attained by the reaction.

TABLE II

COMPOSITION OF THE LOWER BOILING FRACTION

(T in Table I)

	Fraction						
Expt. No.	Monomer (L_1)* 60°C/10 mm.	Dimer (L_2) 73°C/1 mm.	Trimer (C_3, L_3) 105°–10°C/1 mm.		Tetramer (C_4, L_4) 130°–45°C/1 mm.		Residue (R_2) 145°C~/1 mm.
	%P.	%P.	%P.	%Si	%P.	%Si	%P.
1	2	0.5	0	—	21	20.95	6
2	15	11	12	18.3–18.1	9	19.6–19.2	15
3	23	12	11	20.0–18.0	7	19.9–19.6	17
4	27	12	10	17.82	6	18.81	27
5	3	3	8	21.0–20.9	16	21.0–20.8	25
6	2	1	4	—	12	21.1–20.5	27
7	4	1	6	21.00	13	20.8–20.6	30
8	1	1	6	20.95	16	20.61	19
9	8	1	4	17.52	15	21.0–19.9	30

* L_n and C_n indicate the linear n-mer and cyclo-n-mer.
Anal. Calcd. for L_1, L_2, L_3, L_4 and C_n: Si, 13.48, 16.40, 17.67, 18.39 and 20.93% respectively.

(b) *Composition of the hydrolyzate.* (i) *Hydrolyzate obtained from the slow hydrolysis at a constant temperature* (Expt. 1–4).—In Expt. 1–4, hydrolysis was carried out at 0°C, 30°C, 50°C and 70°C by adding chlorosilane slowly (2 g./min.) to the hydrolyzing mixture. In Expt. 1, the trimer fraction was not found and the following plateau was

of monomer (L_1) and dimer (L_2) obtained and the more the contamination of the linear compounds in the trimer and tetramer fractions. It was supposed to be caused by the fission of ethoxy group with temperature. From the distillation curve of Expt. 3, the appearance of C_3 in front of the plateau of the trimer fraction was clearly

shown by its silicon content and a high refractive index at this portion as shown in Fig. 1.

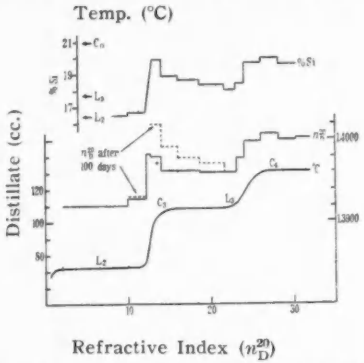


Fig. 1. Distillation curve of Expt. 3 under 1 mmHg.
L_n: Linear n-mer,
C_n: Cyclo-n-mer.

From Fig. 1, C_3 and L_3 may have a close boiling point and it was supposed to be difficult to separate these compounds by the distillation.

(ii) *Hydrolyzate obtained from the rapid hydrolysis* (Expt. 5–9).—From the results obtained in Expt. 1–4, the formation of C_3 was observed, only at the temperature range of 30°C to 50°C and the amount of C_3 was very small by the reaction at the constant temperature. C_3 was successfully obtained without formation of L_3 by the following rapid hydrolysis. The results are given in Table I from Expt. 5 to 9.

By adding the chlorosilane rapidly to the hydrolyzing mixture which was cooled by an ice-salt bath at 0°C, the temperature of the mixture rapidly rose by the reaction. The temperature was observed by the thermometer dipped in the mixture and the highest temperature attained is shown in parentheses in some experiments. After the temperature of the mixture fell down to the temperature of the bath in which ice still remained, stirring was further continued until the chlorosilane odor disappeared completely from the mixture.

In Expt. 5–8, a small amount of L_1 and L_2 was obtained. In the trimer fraction, L_3 was not found, while in the tetramer fraction, C_4 was supposed to be contaminated with a small amount of L_4 at the back part of the plateau. Too rapid addition of chlorosilane to the hydrolyzing mixture as in Expt. 9, may also causes the fission of ethoxy group owing to an instantaneous rise of the reaction temperature, and there was obtained a relatively large amount of L_1 and further only L_3 was found in the trimer fraction and the contamination of L_4 was observed in the tetramer fraction.

(c) *Characterizationof the Cyclopolysiloxanes.*—After redistillation, C_3 was reserved at the room temperature (10°C) and the measurement of its physical properties and analysis were carried out during a week. For the characterization of C_4, the tetramer fractions in Table II having the silicon content 19.6 to 21.1 were gathered and redistilled rigorously through the efficient column described above. To obtain the cyclocompounds higher than C_4, the residues (R_2) of Expt. 5–8 were fractionated as above. The gradually rising plateau (b.p. 148°–150°C/0.3 mmHg) with the distillate (12 cc.), having the silicon content of 20.18 to 20.85%, was obtained. From these data, C_5 may seem to be somewhat contaminated with the neighbouring linear compounds. Properties of these cyclopolysiloxanes are given in Table III.

Stability of the Cyclotrimer.—The cyclotrimer obtained above was sealed in a soft glass ampulla and the refractive index, density and molecular weight were measured after 200 and 300 days. The typical results obtained were as follows.

After days	n_D^{20}	d_4^{20}	Mol. Wt. (in benzene)
—	1.3981	1.0764	398
200	1.4032	1.1083	ca. 1000
300	1.4052	—	—
	(1.4070)*		

* Value obtained after the sample had been left open at room temperature for thirty minuites. This change may be caused by the escaping of some volatile matter formed by the decomposition of C_3, for the weight of the sample in a platinum crucible was reduced by about 3.1% of its weight after two hours.

TABLE III

DIETHOXYCYCLOPOLYSILOXANES

C_n: $((C_2H_5O)_2SiO)_n$

Name	Boiling Point °C/mmHg	Refractive Index n_D^{20}	Density d_4^{20}	Molecular Weight Found* (Calcd.)	%Si Found (Calcd.)
Hexaethoxycyclotrisiloxane (C_3)	106/0.7	1.3982	1.0764	400 (402.6)	20.95 (20.93)
Octaethoxycyclotetrasiloxane** (C_4)	125/0.3	1.4015	1.0971	534 (536.8)	20.99 (20.93)
Decaethoxycyclopentasiloxane (C_5)	150/0.3	1.4042	1.1039	660 (671.1)	20.85 (20.93)

* Cryoscopic measurements in benzene.

** T. Takatani, loc. cit., b.p. 138–40/1.5, n_D^{20} 1.4001 and d_4^{20} 1.0946.

As it was of interest to know the compounds which have been formed by the decomposition of C_3, the sample (10 g.) was carefully fractionated through a semi-micro Stedman column of about 30 theoretical plates after 350 days. About 3% of the volatile compound, 2% of L_2 (b.p. 78°C/1 mmHg) and 20% of the trimer fraction (b.p. 106°C/1 mmHg, n_D^{20} 1.3966 and d_4^{20} 1.0364. Anal. Found: Si, 18.19%) were obtained. From the silicon content, this trimer fraction was supposed to be composed of about 84% of L_3 (Reported: b.p. 107°C/0.8 mmHg[9], n_D^{20} 1.3952[9] and d_4^{20} 1.0301[10]) and 16% of unchanged C_3. The higher fraction could not be obtained until the stil-pot temperature reaches 235°C. The residue was a viscous liquid and the silicon content of it was found to be 22.00%.

With all the samples which were contaminated by C_3, the elevation of the refractive index was also observed. For example, it is shown in Fig. 1 in dotted lines. But the change was not observed by the other compounds within one year.

Analysis of Silicon.—Silicon was determined by decomposing the sample with concentrated sulfuric acid.

9) R. Okawara, T. Tanaka and K. Maruo, This Bulletin, 28, 189 (1955).
10) T. Takatani, *J. Chem. Soc. Japan, Pure Chem. Sec.*, 73, 409 (1952) (in Japanese).

Summary

(1) Diethoxydichlorosilane did not easily react with sodium bicarbonate.
(2) Diethoxycyclopolysiloxanes beginning with cyclotrimer could be obtained from the hydrolysis of diethoxydichlorosilane by using pyridine as an acid acceptor.
(3) The lower members of diethoxycyclopolysiloxanes having three to five silicon atoms have been characterized.
(4) The cyclotrimer was found to be formed only in the limited conditions of hydrolysis and it was decomsosed spontaneously in a sealed soft glass ampulla.

The authors wish their hearty thanks to Dr. Watase for his encouragement during this work.

Department of Applied Chemistry Faculty of Engineering, Osaka University, Osaka

Dielectric Studies on Colloidal Solutions. I. High-frequency Conductivity of Aqueous Solutions of Paraffin-chain Salts

By Michio SHIRAI and Bun-ichi TAMAMUSHI

(Received May 24, 1955)

It is a well-known fact that the equivalent electrical conductivity of aqueous solutions of the various types of paraffin-chain salts shows a sudden fall when the concentration is increased beyond a certain value corresponding to the micelle formation and then, after passing through a minimum point, it increases gradually with increasing concentration. This latter phenomenon was considered by McBain[1] to be due to the change in the dissociation state of the electrolyte contained in micelles. On the other hand, Hartley[2] pointed out that it should come out from the electrostatic interaction.

Some years ago, Schmid and Larsen[3] measured the electrical conductivity of aqueous solutions of some paraffin-chain salts at frequencies of 15 and 25 Mc./sec. by means of Deubner's method[4], and found that the high-frequency effect showed itself at the concentration corresponding to the sudden fall of the equivalent low frequency conductivity. Recently, the authors have investigated the high-frequency conductivities of sodium dodecyl sulphate, sodium oleate, and dodecyl amine hydrochloride at frequencies of 15 and 30 Mc./sec. by means of the resonance method over a wider range of concentration. Our experimental method and result may be useful for further discussion of the problem of micelle structures.

1) J.W. McBain and M.D. Betz, *J. Am. Chem. Soc.*, 57, 1905 (1935).
2) G.S. Hartley, ibid., 58, 2347 (1936).
3) G. Schmid and E.C. Larsen, *Z. Elektrochem.*, 44, 651 (1938).

Experimental

Method of measurement. — The method of measurement lies in the determination of the

4) A. Deubner, *Physik. Z.*, 30, 946 (1929).

width of the resonance curve of a resonant circuit coupled to a high-frequency oscillator[5]. The stabilized oscillator supplies a high-frequency wave of constant amplitude and of fixed frequency to a resonator, to which is connected a valve voltmeter. The block diagram of the whole apparatus is indicated in Fig. 1.

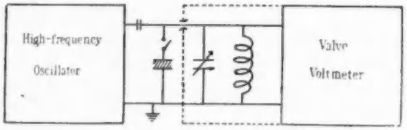


Fig. 1. Block-diagram of the apparatus.

The resonator consists of a parallel plate condenser containing the test liquid parallel to a variable condenser across an inductance. This variable condenser is an eccentric cylindrical one adjusted by a micrometer. The condenser containing the test liquid is immersed in a thermostatically controlled bath. Each part is screened in a metal box. The coupling of the resonator to the oscillator is so loose as to eliminate any pulling of the oscillator by the resonator. The high-frequency voltage of the resonator tuned to the oscillator is measured by the valve voltmeter. The circuit of the valve voltmeter is indicated in Fig. 2. The sensitivity of the galvanometer used is 2.8×10^{-9} amp./mm., and its deflection must be proportional to the square of the input voltage. This can be done by adjusting the grid bias of the valve.

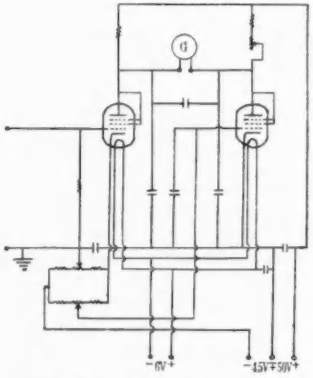


Fig. 2. Circuit of valve voltmeter.

Thus, the shape of the resonance curve for various test liquids placed in the parallel plate condenser is determined. The conductance of the resonator, G, is determined by the following formula[5]:

$$G=\frac{\omega(C-C_R)}{\sqrt{\left(\frac{V_R}{V}\right)^2-1}},$$

where, ω = frequency at which measurement is made.
V_R = voltage at resonance.
C_R = capacitance at resonance.
V = voltage at any other point.
C = capacitance at any other point.

In the manner stated above, the conductances of the resonator both with and without the test liquid in the parallel plate condenser can be determined, the difference of those being the conductance of the test liquid. In order to obtain specific conductivities from these conductances, we need a "cell constant". This can be determined by making use of the aqueous solution of potassium chloride as the standard. The whole operation is repeated for a series of concentrations at each frequency-setting of the oscillator. The probable error of the measurement of conductance at each frequency is $\pm0.2\%$.

Materials. — Sodium dodecyl sulphate was a "pure" sample prepared at Nezu Chemical Laboratory, Tokyo.

Oleic acid was purified from a commercial sample by vacuum distillation. Sodium oleate was prepared by neutralizing pure oleic acid with sodium hydroxide.

Dodecyl amine hydrochloride was obtained by neutralizing dedecyl amine which came from Armour and Co., U.S.A. with hydrochloric acid, which was then recrystallized.

The dissolution and dilution of these substances were made with distilled water free from carbon dioxide and thus solutions of various concentrations were obtained.

Results and Discussion

In Tables I—III and in Figs. 3—5, the high-frequency effects of the three substances under investigation are indicated. Here the high-frequency effect is expressed by

$$H=100\frac{(\Lambda_h-\Lambda_l)}{\Lambda_l},$$

where Λ_l is the low-frequency equivalent conductivity and Λ_h is the high-frequency equivalent conductivity. Λ_l was measured at 700 c./sec. In Figs. 3—5, the low-frequency equivalent conductivity is also shown for comparison.

TABLE I
SODIUM DODECYL SULPHATE
Temp. 25°C

Concentration mol./l.	Equivalent conductivity 700c./sec.	High-frequency Effect 30Mc./sec.	15Mc./sec.
0.0025	79	0	0
0.005	76	0	0
0.008	71	0	0
0.01	60	1.1	0
0.015	46	2.4	0.8
0.025	37	2.5	0.3
0.05	29	2.0	0

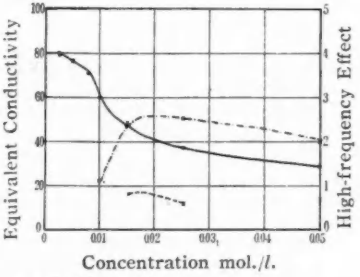
5) Report of the Sub-Committee of Japan Society for the Promotion of Scientific Research, *J. I. E. E. Japan*, **59**, 519 (1939).

TABLE II
SODIUM OLEATE

Concentration mol./l.	Equivalent conductivity 700c./sec.	High-frequency Effect (Temp. 25°C) 30 Mc./sec.	15 Mc./sec.
0.005	52	4.1	1.8
0.0075	42	5.0	2.0
0.01	39	4.5	1.7
0.015	37	3.2	1.3
0.02	34	2.5	1.1
0.025	33	2.2	1.0

TABLE III
DODECYL AMINE HYDROCHLORIDE

Concentration mol./l.	Equivalent conductivity 700c./sec.	High-frequency Effect (Temp. 25°C) 15 Mc./sec.	30 Mc./sec.
0.0008	99	0	0
0.001	96	0.6	0.3
0.0015	85	2.0	1.5
0.0025	60	4.3	2.8
0.005	35	4.0	2.6
0.01	36	2.7	2.3
0.015	44	1.8	1.5



-·-·× 30 Mc./sec.
---× 15 Mc./sec. } high-frequency effect.
——— · 700c./sec. equivalent conductivity.

Fig. 3. Sodium dodecyl sulphate.

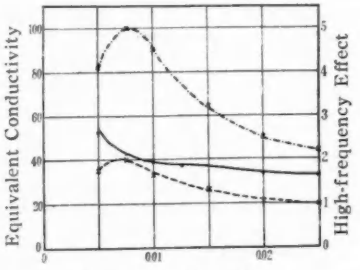


Fig. 4. Sodium oleate.

The Fig. 3 for sodium dodecyl sulphate shows that in the range of very low concentrations the high-frequency effect is very small. We were unable to confirm its existence. But with increasing concentration, the high-frequency effect becomes greater and arrives at its maximum at the concentration where the low frequency equivalent conductivity is decreasing. Then it shows a gradual decrease, but on account of the high conductance of the solution we could not make a measurement at very high concentrations.

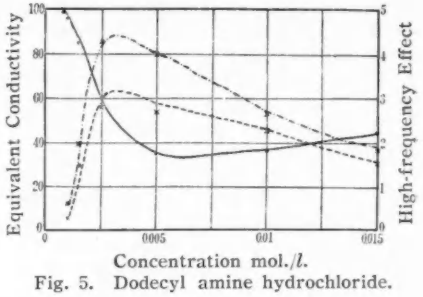


Fig. 5. Dodecyl amine hydrochloride.

The high-frequency effects of sodium oleate and sodium dodecyl amine hydrochloride show similar curves, as shown in Figs. 4 and 5.

The abnormally large values of the high-frequency effect of these solutions at the concentration corresponding to the micelle formation can be interpreted in terms of Debye-Falkenhagen's theory[6] of the dependence of the conductivity on frequency. Of course, the effect of the dielectric relaxation due to the orientation of molecules of the solvent and the solute must be considered, too. The critical frequency of the dielectric relaxation of the water molecule is about 1.5×10^4 Mc./sec., and that of the carboxyl group is about 3×10^3 Mc./sec.[7]. The critical frequencies of the sulphate group and the amino group have not been measured, but it is quite conceivable that they are nearly the same as that of the carboxyl group, considering that these polar groups have nearly the same dimensions. Thus, the critical frequencies of these groups are very high, and therefore the dielectric losses due to their orientation are negligible at frequencies of 15 and 30 Mc./sec., at which our measurement has been performed. Moreover, as molecules contained in a micelle may be rather in a liquid state of aggregation as is shown from the solvent properties of the micelle[8], the orientation of the micelle itself may not take place.

According to Debye-Falkenhagen's theory, the high-frequency effect incraeses with in-

6) P. Debye and H. Falkenhagen, *Physik. Z.*, **29**, 121, 401 (1928); *Z. Elektrochem.*, **34**, 562 (1928).
7) T.J. Buchanan. *J. Chem. Phys.*, **22**, 578 (1954).
8) cf. A.E. Alexander and P. Johnson, "Colloid Science", Oxford Press (1949), p. 685.

creasing valency of the electrolyte. Considering that ions in the solution under investigation join into a polyvalent ion on account of the formation of micelles, the high-frequency effect can be fairly great in the solutions under investigation, in spite of the loose structure of micelles. The critical fall of the low-frequency equivalent conductivity is probably due to this electrostatic interaction which comes into play with the formation of polyvalent micelle ions.

With further increasing concentration, the high-frequency effect shows a gradual decrease, as shown in Figs. 3—5. This decrease may be partly due to the shortening of the relaxation time of the ionic atmosphere with the increase of concentration, it being impossible to detect the effect at the frequency corresponding to the relaxation time at the applied frequency of 30 Mc./sec.. However, as shown in Fig. 5, there are cases where the low-frequency equivalent conductivity gradually increases with increasing concentration, and in order to account for the dependence of the low-frequency equivalent conductivity and that of the high-frequency effect on concentration consistently, we must conclude that the electrostatic interaction decreases as a whole with the concentration. Such reduction of the electrostatic interaction is presumably due to a loosening of counter ions due to the overlap of ionic atmospheres and consequently a change in the structure of micelles with increasing concentration.

Summary

The high-frequency conductivity of solutions of sodium dodecyl sulphate, sodium oleate, and dodecyl amine hydrochloride was measured at frequencies of 15 and 30 Mc./sec.. The high-frequency effect remarkably appeared at the concentration corresponding to the critical micelle concentration and the effect can be interpreted in terms of Debye-Falkenhagen's theory of strong electrolytes.

The appearance of maximum and gradual decrease in high-frequency effect may be explained by the shortening of the relaxation time or by the reduction of the electrostatic interaction due to the change of micelle structures with the increase of concentration.

We are grateful to Nezu Chemical Laboratory, Tokyo and Armour & Co. U. S. A. for their kind supply of samples of detergents. A part of the expense for the experiment has been defrayed from a grant given by the Ministry of Education.

Chemistry Department, College of General Education & Institute of Science and Technology, The University of Tokyo, Tokyo

Diffusion of Hydrocarbon, Alcohols and Esters through the Aqueous Solutions of Cationic Detergent

By Haruhiko OKUYAMA

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Introduction

There have been many reports since the Graham-age about the diffusion of solute in colloidal solutions, for example through gelatine or agar solution. In these cases, it has been shown that the velocity of diffusion is only slightly affected in the presence of gelatine if the solute molecules or ions are small and non-reacting with them, but deeply influenced if there are interactions between the solute and the gelatine[1].

1) T. Graham. *Liebig Ann.*, **121**, 1 (1862); L. Friedman and E.O. Kraemer, *J. Am. Chem. Soc.*, **52**, 1295, 1305, 1311 (1930).

Investigations have been made in this paper, as to how the diffusion of a certain substance is influenced by the presence of a detergent. In general the detergent has an amphipathic structure, which is composed by hydrophilic and oleophilic part in the molecule. According to this amphipathic property, they associate in the aqueous solution and micelle formation occurs. The association occurs between not only detergent molecules themselves but also the other substances added to the solution, for instance, non-polar compounds such as hydrocarbon occupying the non-polar loci of micelles, viz. inside the micelles, resulting in swollen micelles. On

the other hand the polar compounds such as alcohol take a position which is essentially similar to the detergent molecules which make up the micelles.

It will be expected in this case that the kinetic unit is different according to the absence or presence of a detergent. In the latter case the diffusion is considerably delayed. Some results have been reported by Dean and Vinograd[2] in regard to the diffusion of solubilized dyes in Aerosol OT micelles, where diffusion was measured through sintered glass and cellophane membrane. However, this porous disc method has disadvantages in many respect and the solubilizate also has a complicated chemical structure in their experiments. In this paper the diffusion of some simple compounds in detergent solution has been investigated by the free boundary method which is much more free from theoretical objection.

Experimental Methods and Samples

The diffusion coefficient was measured in 2.37% aqueous solution of trimethyldodecylammonium chloride (TMDA). This sample was the pure grade product of Nihon Yushi Co. To obtain the concentrated aqueous solution, TMDA was dialysed[3] by cellophane membrane to remove the low molecular substances or ions supposed to be contained in this sample. Some TMDA escaped through the membrane but the portion retained was pure enough for our present purpose. The solution inside the membrane was diluted to 2.37% by weight, of which relative viscosity was 1.352 and pH was about 5.4. The diffusing substances which were recrystallized or redistillated before use were of the highest market grade.

The diffusion coefficient was measured by the method of refractive index. The diffusion-cell was Neurath-type, made of Ni-Cr stainless steel 18-8 manufactured by Kobe Steel Factory, the thickness being 30 mm. The optical system was the diagonal Schlieren type, the same as described in other papers[4]. The cell was placed in a thermostat at 25.0°C More than ten diffusion patterns (concentration-gradient curves) were photographed at almost the same time intervals in each experiment. In the case of the most rapid diffusion the time interval was about three minutes while it was about an hour for the slowest one. The diffusion coefficient was calculated from the breadth between two inflection points in diffusion pattern whose ordinate could easily be found from the maximum height of the pattern[5].

2) R.B. Dean and J.R. Vinograd, *J. Phys. Chem.*, **46**, 1091 (1942).
3) J.T. Yang and J.F. Foster, *J. Phys. Chem.*, **57**, 628 (1953); B.S. Harrap and I.J. O'Donnell, *J. Phys. Chem.*, **58**, 1099 (1954).
4) N. Sata, H. Okuyama and K. Tyuzyo, *Kolloid-Z.*, **121**, 46 (1951); H. Okuyama and K. Tyuzyo, This Bulletin, **27**, 259 (1954).
5) H. Neurath, *Chem Rex.*, **30**, 357 (1942).

Results and Some Considerations

(1) Experiments with completely soluble solute in water. — In Table I, the diffusion coefficients of some solutes in water and in the TMDA solution are listed.

TABLE I
DIFFUSION COEFFICIENTS OF SOME SOLUBLE SUBSTANCES IN TMDA-SOLUTION AND IN WATER

Substance	C_1	C_2	$D_s \times 10^7$ cm²/sec.	$D_w \times 10^7$ cm²/sec.
Urea	2.0%	1.0%	137	135
Fructose	0.1%	0.0%	76.0	73.4
Potassium Chloride	0.1N	0.0N	202	192

C_1 and C_2 show the initial concentration of the solute in lower and upper solutions on the diffusion cell respectively. D_s and D_w indicate the diffusion coefficient of the solute in TMDA 2.37% solution and in water respectively.

The equation of Onsager and Fuoss[6]

$$D = \frac{RT}{f}\left(1 + \frac{d \ln \gamma}{d \ln c}\right)$$

was derived from a general treatment of the diffusion problem which may be used to explain the above results. In this equation, f is the frictional coefficient and γ, the activity coefficient, c the concentration of the solute. The hydrodynamic factor, f and the thermodynamic factor, $\frac{d \ln \gamma}{d \ln c}$ also may be increased by the presence of TMDA. It is thus seen that both factors approximately may cancel one another and roughly account for the fact that D_s differ only slightly from D_w as seen in Table I. Similar phenomena are reported[7] in which the diffusion coefficients of certain high-polymer solutions are not sensitively dependent on concentration, since hydrodynamic and thermodynamic factors both increased with the concentration of the high polymer. Potassium chloride affects the state of micelles greatly[8], however this has no relation to the present subject.

(2) Experiments with nonpolar substance. —The diffusion coefficient of hexane solubilized in TMDA solution is shown in Table II.

The diffusion coefficient is far less than that of Exp. 1. At the constant concentration gradient, D_s becomes somewhat greater as the concentration of hexane decreases

6) L. Onsager and R.M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).
7) C.O. Beckmann and J. L. Rosenberg, *Ann. N. Y. Acad. Sci.*, **46** (5), 329 (1945).
8) v.g. P. Debye and E.N. Anacker, *J. Phys. Chem.*, **53**, 1 (1949).

TABLE II

DIFFUSION COEFFICIENTS OF HEXANE SOLUBILIZED IN TMDA-SOLUTION

C_1	C_2	$D_s \times 10^7$ cm²/sec.	$(D_1-D_2)\times 10^7$ cm²/sec.
0.1%[9]	0.6%[9]	1.90	1.62
0.3	0.8	1.68	1.50
0.5	1.0	1.30	1.37
0.7	1.2	1.31	1.25
1.0	1.5	0.98	1.07
0.1	1.0	3.00	2.69
0.5	1.5	2.72	2.44
0.1	1.5	4.21	3.76

micelles completely. For the same reason as mentioned above the radius of the swollen micelle cannot be obtained directly.

From the X-ray data[10] it is supposed that the diameter of the micelle of TMDA is about 35 Å and the diameter of the swollen micelle is increased linearly with the solubilized amount of solubilizate. The maximum (saturated) increment is reported to be 15 Å. In this experiment 1.5% hexane solution is nearly the saturation-value.

Assuming that the X-ray data also hold in this experiment, we can calculate the true diffusion coefficient as shown in Table III.

TABLE III

CALCULATED RADII AND DIFFUSION COEFFICIENTS OF THE SWOLLEN MICELLES BY HEXANE

Hexane %	0.0	0.1	0.3	0.5	0.6	0.7	0.8	1.0	1.2	1.5
r(A)	17.5	18.0	19.0	20.0	20.5	21.0	21.5	22·5	23.5	25.0
$D\times 10^7$	13.88	13.49	12.80	12.17	11.87	11.57	11.30	10.80	10.32	9.73

and D_s considerably increases with increasing concentration gradient of hexane.

In these cases the kinetic units of diffusion must exclusively be micelles swollen by hexane molecules, because the hexane molecules exist only in solubilized micelles and the molecularly dispersed hexane is negligible. The homogenization of hexane-containing micelles must occur initially in such a manner that the more swollen micelles sink and the less swollen micelles rise. Then the observed diffusion coefficient in Table II may be considered as the difference of the diffusion coefficients of both micelles in water.

Assuming the micelle as spherical, the relation between the radius of the micelle and diffusion coefficent is shown by Einstein and Sutherland, as follows:

$$D=\frac{RT}{6\pi\eta rN} \qquad (1)$$

R represents gas constant, T, absolute temperature, η, solvent viscosity, N, Avogadros' number, D, diffusion coefficient and r, radius of diffusing particles. Evaluating Eq. (1), we obtain.

$$rD=2.43\times 10^{-13}\ \text{C.G.S.} \qquad (2)$$

The radius of the micelle can be calculated from Eq. (2) by the measurement of the difusifon coefficient alone of the TMDA solution. However the diffusion coefficient cannot be obtained owing to the influence of diffusion potential caused by the charged large micelles and small gegenions. On the other hand, in order to suppress this potential it is necessary to add sufficient amounts of electrolyte, which would change the state of

From Table III the difference between two diffusion coefficients of swollen micelles at C_1 and C_2 can be obtained, and the values (D_1-D_2) are listed in the last column of Table II. Fairly good coincidence with the experimentally obtained diffusion coefficients is found.

(3) **Experiments with polar compounds.**— Table IV exhibits the diffusion coefficients of alcohols in TMDA- solution.

TABLE IV

DIFFUSION COEFFICIENTS OF VARIOUS ALCOHOLS IN TMDA-SOLUTION

Alcohols	C_1	C_2	$D_s\times 10^7$ cm²/sec.	Solubility[11] in water
n-Amyl-	1.0%[9]	2.0%[9]	15.8	2.20
n-Octyl-	1.0	2.0	6.15	0.059
n-Lauryl-	1.0	2.0	0.915	0.00
n-Lauryl-	0.1	1.0	4.87	0.00

The diffusion coefficient of iso-amylalcohol in water is 93.2×10^{-7}cm²/sec. So n-amylalcohol diffuses much more slowly in the detergent solution than iso-amylalcohol in water in spite of the same molecular weight.

In Table IV, it is seen that the longer the chain length of alcohol the slower is the diffusion velocity. In these cases, however, the solubility in water has a somewhat closer relation to the diffusion velocity than the chain length of alcohols. The concentration gradient curves of diffusion obtained from n-amylalcohol deviate remarkably from the ideal Gaussian curves and assume the shape

9) volume %

10) W.D. Harkins, R.W. Mattoon and M.L. Corrin, *J. Colloid Sci.*, **1**, 105 (1946). W. D. Harkins, R. W. Mattoon and R. S. Stearns, *J. Chem. Phys.* **15**, 209 (1947); **16**, 646, 652 (1948).

11) Grams of the substances in 100 g. water.

of two (at least) ideal curves superimposed, of which one is very sharp and the other very diffuse. The diffused one may be caused by simple alcohol molecules and the sharp one by complicated mixed micelles composed of alcohol and detergent molecules.

The present method of calculating the diffusion coefficient gives only the complex average value of two different diffusion coefficients of these. It is impossible to analyze the value in greater detail at the present stage.

If there were rapid equilibrium between amylalcohol in swollen micelles and that in the extra-micellar solutions, diffusion would be performed chiefly by molecularly dissolved *n*-amylalcohol; then the concentration-gradient curves would show a different patterns.

Therefore, the sorption or desorption of dissolved alcohol molecules by micelles may not occur so easily in this case as Winsor's equilibrium theory[12] of micelles suggests. The slow exchange between swollen micelles and solutes may be similar to the phenomena of surface aging which exhibit hindered diffusion to the surface by monomolecular film of surface active substances[13].

Laurylalcohol diffuses like hexane but in this case the circumstances are more complex owing to the penetration and the least diffusion coefficient value and the highest viscosity, has been obtained presumably as the result of large sandwich-micelles.

In Table V, the diffusion coefficients of esters are listed. The hydrolysis was not observed at least.

TABLE V

DIFFUSION COEFFICIENTS OF VARIOUS ESTERS IN TMDA-SOLUTION

Esters	C_1	C_2	$D_s \times 10^7$ cm²/sec.	Solubility[11] in water
Ethylacetate	1.0%[9]	2.0%[9]	102	7.56
Butylacetate	1.0	2.0	15.9	2.3
Dimethylphthalate	1.0	0.5	18.2	0.24
Diethylphthalate	1.0	0.5	8.25	—
Dibutylphthalate	1.0	0.5	4.36	—

Ethylacetate which is completely soluble at this concentration diffuses ordinarily, but D_s of butylacetate is very small and the concentration gradient curves of diffusion of this are the composite curve of at least two parts just as in the case of *n*-amylalcohol mentioned above.

12) P.A. Winsor, *J. Phys. Chem.*, **56**. 391 (1952).
13) A.F.H. Ward and L. Tordai, *Rec. Trav. Chim. Pays-Bas*, **71**, 396, 482, 572 (1952); A.E. Alexander and P. Johnson, "Colloid Science", Clarendon press, Oxford 1949, p. 529.

McBain found unusual behaviours in the case of solubilization of dimethylphthalate[14] in detergent solution which is insoluble both in water and in hydrocarbon and suggested that the rearrangement of micelles takes place and the solubilization of dimethylphthalate molecules is achieved by polar groups of small micelles. In such a case it will be expected that the circumstances are somewhat different in diffusion process. But the numerical value of the diffusion coefficient on Table V shows no anomaly. A parallelism is rather found between the solubility and the diffusion coefficient. McBain took up dimethylphthalate only, diethylphthalate and dibutylphthalate are also investigated in these experiments.

In Table VI the diffusion coefficients of partly water-soluble polar substances in various mean concentrations are listed.

TABLE VI

CONCENTRATION DEPENDENCE OF DIFFUSION COEFFICIENTS IN TMDA-SOLUTION

	C_1	C_2	$D_s \times 10^7$ cm²/sec.
n-Amylalcohol	1.0%[9]	2.0%[9]	15.8
	2.0	3.0	11.8
	3.0	4.0	6.22
n-Butylacetate	0.5	1.5	15.9
	1.0	2.0	15.1
	2.0	3.0	12.6
	3.0	4.0	9.75
	4.5	5.5	5.76
Ethylacetate	1.0	2.0	102
	3.0	4.0	93.8
	5.0	6.0	86.1
	7.0	8.0	63.4
	8.0	10.0	22.4
	10.0	13.0	15.7
Dimethylphthalate	1.0	0.5	18.2
	1.5	0.5	15.6
	2.7	1.5	5.16

These polar compounds dissolve somewhat in water but in the detergent solution much more through solubilization. The higher the concentration of these polar compounds, the smaller becomes the valueof the diffusion coefficient. This is explained by assuming that the contribution of complicated micelles to the diffusion becomes more dominant compared with the single molecules of the solute as the concentration is increased. This is also found in the diffusion curve since the diffuse part of the diffusion pattern tends to vanish as the concentration of the solute approaches saturation.

14) J.W. Mc Bain and Mc Han, *J. Am. Chem. Soc.*, **70**, 3838 (1948).

No quantitative relation between concentration and diffusion coefficient can be found, since the obtained diffusion coefficient is a complicated mean of two components.

Summary

(1) Urea, fructose and potassium chloride which are completely soluble in water, diffuse in the TMDA solution at about the same rate as in water notwithstanding the fact that the former has higher viscosity than the later.

(2) The diffusion coefficient of hexane is in a fairly good coincidence with the difference of the calculated diffusion coefficient from X-ray data between more and less swollen micelles.

(3) The diffusion of alcohols and esters is generally governed by their solubility in water. From the concentration gradient curves of diffusion, they are considered to diffuse on two different mechanisms, one as the single molecule and the other as the complex group associated with the detergent micelles.

(4) The equilibrium between solute in micelles and in water is rather slower process when the mechanical disturbance or convection is absent in the solution.

(5) The anomalies reported on the solubilization of dimethylphthalate is not observed in these diffusion experiments.

In conclusion, the author thanks Prof. Dr. N. Sata for his kind instruction and also expresses sincere thanks to Mr. Y. Seno of Nihon Yushi Co. who afforded valuable samples and suggestions.

Department of Chemistry, Faculty of Science, Osaka University, Osaka

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*A Kinetic Study on the Vinylation of Alcohol**

By Teiji TSURUTA, Hiroyuki KOMATSUBARA and Junji FURUKAWA

(Received May 23, 1955)

Previous interpretations[1] of the vinylation reaction of alcohol are not satisfactory, because few of them are based upon kinetic studies. In the present study, the course of the vinylation was traced under atmospheric pressure using phenylacetylene and benzyl alcohol as reactants, so that inaccuracies inherent in the autoclave reaction were eliminated.

In the first place, it was synthetically ascertained that the acetylene and the alcohol react to give a corresponding vinylation product, styryl benzyl ether, under a condition similar to that in the present kinetic measurement. Secondly, the volumetric analysis of phenylacetylene was examined and modified. Thirdly, dependences of the rate of reaction upon the concentration of phenylacetylene and the activity of the alcoholate were examined. And finally, a possible mechanism of the vinylation is proposed.

* Presented at the 7th Annual Meeting of the Chemical Society of Japan in Tokyo, April 2, 1954.

1) A review on the vinylation mechanism: S. Murahashi, *J. Soc. Org. Synth. Chem. Japan*, **10**, 485 (1952) (in Japanese).

Experimental

1. Materials.—Commercial C.P. benzyl alcohol was treated with anhydrous potassium carbonate and rectified at a reduced pressure under nitrogen. A cut boiling at 110–111°/30 mm. was used. Phenylacetylene was prepared from cinnamic acid according to the literature[2]. A cut boiling at 50–51.5°/30 mm. was used.

2. Styryl benzyl ether.—A solution of 2 g. of metallic sodium in 125 g. of benzyl alcohol was placed in a 500-cc. four-necked flask equipped with a stirrer, thermometer, reflux condenser and dropping funnel. The solution was heated to 130°C in an oil bath and 20 g. of phenylacetylene in 50 g. of benzyl alcohol was added. The addition was controlled so that the temperature of the solution did not exceed 135°C. After being stirred at that temperature for two hours, to the solution was added 100 cc. of water and the separated organic layer was extracted with ether. The ether layer was washed with water, dried on anhydrous potassium carbonate, the solvent evaporated and the residue was distilled in vacuo under nitrogen. Thus, besides unreacted phenylacetylene, 23 g. of an oily product (A) boiling at

2) H. Gilman, "Organic Syntheses, Collective Vol. I", John Wiley and Sons, Inc., New York, N.Y. (1948), p. 438.

183°/9 mm. was obtained. A small quantity of residue remained in the distillation flask. On being cooled, the adduct (A) solidified into white crystals which showed m.p. 72–73°C on being recrystallized three times from ethanol.

Anal. Found: C, 85.68; H, 6.68; Mol. Wt., 203. Calcd for $C_{15}H_{14}O$: C, 85.71; H, 6.67; Mol. Wt., 210.

3. A Modified Volumetric Analysis of Phenylacetylene.—The principle[3] of the analysis is represented as

$$C_6H_5C{\equiv}CH+Cu^{(+)} = C_6H_5C{\equiv}CCu+H^{(+)} \quad (1)$$

$$C_6H_5C{\equiv}CCu+Fe^{(3+)}+H_2SO_4 = C_6H_5C{\equiv}CH+CuSO_4+Fe^{(3+)}+H^{(+)} \quad (2)$$

$$10Fe^{(3+)}+2KMnO_4+8H_2SO_4 = K_2SO_4+2MnSO_4+10Fe^{(3+)}+5SO_4^{(2-)}+8H_2O \quad (3)$$

1 mol. of $C_6H_5C{\equiv}CH$ (102.13 g.) corresponds to 1 N $KMnO_4$ (31.606 g.).

Since cuprous chloride in saturated ammonium carbonate solution[4] was found to give poor results for the precipitation reagent of phenylacetylene, we applied Ilosvay's method[3] with some modifications to the present analysis.

A solution of 1 g. of $CuSO_4{\cdot}5H_2O$ in 5 cc. of water was added to 5.5 cc. of 10.61 N NH_4OH. Into this deep blue solution, 3 g. of $NH_2OH{\cdot}HCl$ was dissolved and diluted with water to 50 cc. The blue color disappeared completely in a few minutes[5].

The precipitation of the acetylide was seriously affected by the concentration of NH_4OH. The most suitable pH for the precipitation was found to be 8.6–8.7. To examine the accuracy of the analysis, known quantities (9.039, 4.520, 1.792 and 0.897 ($\times10^{-4}$ mol.)) of the acetylene in 5 cc. of ethanol were treated with 20 cc. of the cuprous solution. The yellow precipitates of the acetylide were filtered on a glass filter (No. 4). To remove the excess hydroxylamine, the precipitates were washed with water several times until the filtrate did not decolorize one drop of N/10 $KMnO_4$. During these operations, the precipitates should be covered with the mother liquid in order to keep the acetylide from the air oxidation.

For dissolving the precipitates, a solution of ferric sulfate in sulfuric acid was prepared; 100 g. of ferric sulfate[6] was dissolved in 250 g. of sulfuric acid (sp. gr., 1.85), which was diluted with water to 1 l. Twenty cc. of the ferric solution was mixed with 10 to 15 cc. of H_2SO_4, added to the precipitates and was digested for 10 to 20 minutes on a steam bath to complete solution. There was obtained a clear light-green solution involving ferrous ion, which was cooled to the room temperature, and to this was added a few cc. of 85% phosphoric acid[7], and then titrated with N/20 $KMnO_4$. The average of errors for 16 measurements was −0.8% with standard deviation 4.12%.

For the precipitation of the acetylide from benzyl alcohol solution some modifications were required because of the slight solubility of the alcohol in water. Known quantities (10.626, 5.313 and 2.125 ($\times10^{-4}$ mol.)) of phenylacetylene in 10 to 15 cc. of benzyl alcohol were mixed with 20 to 30 cc. of the precipitating agent under vigorous shaking. The mixing was effected by the addition of some ethanol. When the precipitation was completed, the precipitates were filtered and washed successively with water, aqueous ethanol, and with ethanol and water to remove hydroxylamine and benzyl alcohol. The average of errors for 11 measurements was −0.51% with standard deviation 4.96%.

4. Kinetic Measurement.—The reactions were carried out in test tubes immersed in an oil bath, the temperature of which was controlled to 130±0.5°C. A typical run of the measurements is as follows:

A 5.4-cc. solution of sodium benzylate in benzyl alcohol was placed in a 15-cc. test tube and heated to 130°C. To this solution, a 5-cc. solution of phenylacetylene in benzyl alcohol was added. The initial concentrations of phenylacetylene, sodium benzylate and benzyl alcohol were 0.001, 0.010 and 0.100 (in mol. ratio), respectively. After a definite time interval, the reaction solution was added to a slight exess 1 N HCl solution to interrupt the reaction. The excess of hydrochloric acid was neutralized with 1 N NaOH using methyl red as indicator and the unreacted phenylacetylene in the mixture was analyzed. In one run, the analysis was done with respect to four to eight test tubes with the reaction time varied.

Results and Discussion

The results obtained are summarized in Table I. The rates of vinylation estimated

TABLE I

REACTION BETWEEN PHENYLACETYLENE* AND BENZYL ALCOHOL IN BENZYL ALCOHOL AT 130±0.5°

Exp. No.	Sodium Benzylate (M)	(a_r)	$k_1=v/p$ ($\times10^{-2}$)	$k_2=k_1/a_r$ ($\times10^{-2}$)	No. of Tests
1	0.48	2.17	1.34±0.08	0.66	7
2	.72	3.50	2.33±0.03	.67	7
3	.86	4.85	4.36±0.32	.90	7
4	.87	4.93	4.91±0.19	.99	7
5	.97	6.35	5.75±0.07	.91	6
6	1.00	6.97	6.75±0.14	.97	4
7**	1.01	7.01	6.73±0.19	.96	6
8	1.04	7.95	7.28±0.34	.92	4
9	1.13	10.77	9.05±0.14	.84	5
10	1.37	20.35	17.71±0.77	.87	5
				Mean: 0.87±0.08	

* The initial concentration p_0 of the acetylene is 0.096 mol./l.

** p_0: 0.048 mol./l.

3) L. Ilosvay and N. Ilosva, *Ber.*, **32**, 2697 (1899).

4) Fr. Hein, A. Meyer, *Z. anal. Chem.*, **72**, 30 (1927).

5) The solution should be kept from contact with air. In this study, the solution was prepared immediately before the analysis.

6) The ferric alum solution, which appeared in Hein's paper[4] as the reagent for solution of the acetylide, was not satisfactory, because it was difficult to obtain a clear ferric solution even if sulfuric acid was used in great excess.

7) F.P. Treadwell, "Lehrbuch der anal. Chem. II. Band", Franz Deuticke, Leipzig (1937), p. 523.

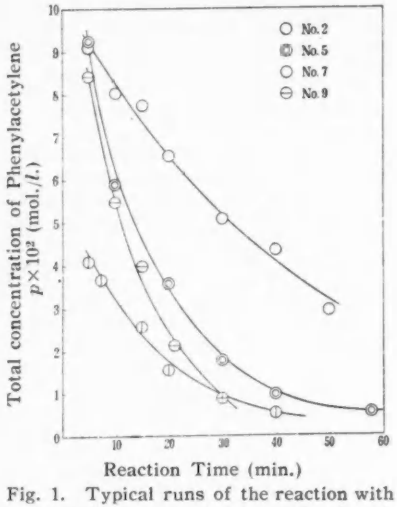


Fig. 1. Typical runs of the reaction with the initial concentration of phenylacetylene 0.096 (mol./l.)[a]. The concentrations of sodium benzylate: 2) 0.72; 5) 0.97; 7) 1.01; 9) 1.13 (mol./l.)

[a] In No. 7, the initial concentration of the acetylene is 0.048 (mol./l.).

from straight line portions of the reaction curves, some examples of which are shown in Fig. 1, were found to be first order with respect to the total concentration of the acetylene as shown in Table I. Thus the rate v is expressed as

$$v = k_1 p \tag{4}$$

where p denotes the total concentration of phenylacetylene and k_1 is a constant. From Table I, it can be seen that the constant k_1 is proportional to the relative mean ionic activity[8] a_r of the alcoholate but not to the analytical concentration. Thus Eq. (4) is reduced to Eq. (5):

$$v = k_2 p a_r \tag{5}$$

where k_2 is a constant.

If we assume that the addition of the alcoholate ion to the acetylene is the rate determining stage, the rate v of the vinylation is expressed as Eq. (6).

$$v = k_3[RO^{(-)}][R'C{\equiv}CH] \tag{6}$$

where k_3 is a constant. In the reaction system, an equilibrium between the alcoholate and the acetylide is present:

$$RO^{(-)} + R'C{\equiv}CH \underset{}{\overset{K_1}{\rightleftarrows}} ROH + R'C{\equiv}C^{(-)} \tag{7}$$

where K_1 is an equilibrium constant, and

$$[RO^{(-)}] + [R'C{\equiv}C^{(-)}] = [Na] \tag{8}$$

$$[R'C{\equiv}CH] + [R'C{\equiv}C^{(-)}] = p \tag{9}$$

From Eqs. (6)—(9),

$$v = k_3 p[Na][ROH]^2/\{[ROH] + K_1[RO^{(-)}]\}\{[ROH] + K_1[R'C{\equiv}CH]\} \tag{10}$$

Under the present condition, the reaction was carried out in benzyl aclohol in large excess, so that Eq. (10) is reduced to

$$v = k_4 p[Na] \tag{11}$$

where k_4 is a constant. Since the relative mean ionic activity a_r of sodium benzylate is little varied under the condition even if the formation of acetylide is taken into consideration, Eq. (11) is equivalent to Eq. (5)[9]. These results are essentially in accordance with Rigamonti and Bernardi's[10].

In a previous paper[11], we reported a rate expression:

$$v = k[Ac.]^{1.5}[Na]^1[Al.]^{1.4} \tag{12}$$

where Ac. and Al. denote acetylene and ethanol. The reaction was examined with low concentration of sodium alcoholate so that Eq. (10) was transformed to Eq. (13).

$$v = k_3 p[Na][ROH]/\{[ROH] + K_1[R'C{\equiv}CH]\} \tag{13}$$

Equation (12) was interpreted by Eq. (13).

Recently Otsuka[12] found that the dependence of the rate upon the concentration of alcohol or of acetylene decreased, to a degree less than first order, with increasing concentrations of the reactants. He accounted for the kinetic data in terms of a complex formation from acetylene, alcohol and alcoholate. However, there seem to be no experimental evidences for such complex intermediates.

In his experiment, the concentration of the alkali is so small that Eq. (13) still holds well. Considering the order of magnitude of pK_a[13], the tendency of decrease in the reaction order of alcohol or of acetylene is well accounted for by Eq. (13).

Equation (5) may be derived from an alternative mechanism in which an addition between benzyl alcohol and phenylacetylide is assumed as the rate determining step.

8) The relative mean ionic activity a_r of the alcoholate in benzyl alcohol was potentiometrically determined according to the Harned method:
a) H.S. Harned and J. C. Hecker, *J. Am. Chem. Soc.*, **55**, 4838 (1933).
b) H.S. Harned and M.A. Cook, ibid., **59**, 496 (1937).

9) $[Na] = k_5 a_r$

10) R. Rigamonti and L. Bernardi, *Chime. Ind. (Milan)*, **34**, 561 (1952); *C.A.*, **47**, 2583b (1953).

11) A. Onishi, N. Saito and J. Furukawa, *Repts. Chem. Research. Inst., Kyoto Univ.*, **19**, 85 (1949) (in Japanese).

12) S. Otsuka, presented at the 8th Annual Meeting of the Chemical Society of Japan in Tokyo, April 1, 1955.

13) For example, pK_a of phenylacetylene and benzyl alcohol are 21 and 19. J.B. Conant and G.W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932).

Otsuka[14] found that the rate of vinylation of phenol was much slower than that of alcohol; if a mixture of alcohol and phenol was reacted with acetylene in the presence of alkali, only phenol was vinylated until the latter[15] was completely converted to the vinyl ether. This supports the assumption that alcoholate and acetylene participate in the rate determining step.

Summary

To elucidate the vinylation mechanism, a liquid phase reaction between phenylacetylene and benzyl alcohol was kinetically studied. The reaction was found to proceed along a second order mechanism between the acetylene and the alcoholate. A possible mechanism of the reaction was proposed.

The authors are grateful to Dr. S. Otsuka for private communications and discussion and to Professor S. Okada, Professor S. Yoshizawa and Mr. Hine for their help with the electrochemistry. This work was supported by a grant in aid for Miscellaneous Scientific Research from the Ministry of Education.

Institute for Chemical Research, Kyoto University, Takatsuki, Osaka

14) S. Otsuka, private communication.

15) In the reaction mixture, the concentration of $C_2H_5O(-)$ is negligibly small compared with that of $C_6H_5O(-)$.

The Interaction of Gelatin Molecule with Surface Active Ions

By Kunio TAMAKI and Bun-ichi TAMAMUSHI

(Received May 24, 1955)

Introduction

The interaction between proteins and synthetic detergents has been the subject of discussion of many investigators[1]. It has been reported that the interaction depends upon some factors, among which the ratio of detergent to protein seems to be of importance in elucidating its mechanism[2]. It has also been observed that cationic detergents precipitate only anionic proteins, namely, proteins on the alkaline side of the isoionic point, while anionic detergents precipitate only cationic proteins, namely, proteins on the acidic side of the isoionic point, and that the precipitate initially formed is dissolved when excess detergent is added. Pankhurst and Smith[3] assumed, basing their assumption on their investigation of the complex formation between gelatin and sodium dodecyl sulphate, that the precipitation took place when the monolayer of dodecyl sulphate ions was formed at basic groups of gelatin molecules and the precipitate was led to dissolve when the second adsorption layer was built up. Lundgren[4] also suggested such a mechanism of complex formation between proteins and detergents. Furthermore it has been evidenced that certain stoichiometric combinations can also take place between cationic detergents and proteins on the acidic side of an isoionic point as well as between anionic detergents and proteins on the alkaline side of the isoionic point[5,6,7,8,9].

In this paper we describe our experiment on the interaction of dodecyl amine hydrochloride and sodium dodecyl sulphate on gelatin at various values of hydrogen ion concentration, whereby we studied the phenomena first by determining the combined detergent to the precipitated gelatin and then by measuring flow properties of the mixed solutions.

Experimental

Materials.—The sample of gelatin used in this experiment was a commercial one, its ash content

1) F.W. Putnam, "Advances in Protein Chemistry", 4, 80 (1948).

2) F.W. Putnam and H. Neurath, *J. Am Chem. Soc.*, 66, 692 (1944).

3) K.G.A. Pankhurst and R. C. M. Smith, *Trans. Faraday Soc.*, 40, 565 (1944); 41, 630 (1945); "Surface Chemistry" London (1949) p. 109.

4) H. P. Lundgren, *Textile Research J.*, 13, 335 (1945).

5) H.P. Lundgren, D.W. Elam and R.A. O'Connell, *J. Biol. Chem.*, 149, 183 (1943).

6) F. W. Putnam and H. Neurath, ibid., 159, 195 (1945).

7) H. Neurath and F.W. Putnam, ibid., 160, 397 (1945).

8) S.N. Timasheff and F.F. Nord, *Arch. Biochem. Biophys.*, 31, 309 (1951).

9) B.S. Harrap and J.H. Schulman, *Discussions Faraday Soc.*, No. 13, 197 (1953).

having been found to be 2.6% and the pH of its solution 5.3. This sample was purified by using ion exchange resins by which means the ash content of the gelatin was reduced to less than 0.09% and the pH at the isoionic point of the purified gelatin was found to be 4.8.

Dodecyl amine hydrochloride (DAH) was prepared from dodecyl amine supplied by Armour and Co. U.S.A., and recrystallized twice from acetone.

Sodium dodecyl sulphate (SDS) was a sample of the highest purity supplied by Nezu Chemical Laboratory, Tokyo.

Method of Analysis of Detergents.—SDS which remained uncombined in the mixed solutions was determined by volumetric precipitation process using DAH as a precipitant and eosin as an indicator. DAH was determined in the same manner by using SDS as a precipitant and rhodamin 6G as an indicator. In both cases, the concentration of the standard solutions was 0.001 mole per liter, and the end point of titration was determined by means of the disappearance of fluorescence of these indicators. Such method of analysis had been proposed by the investigators of Nezu Chemical Laboratory[10] and was proved to be applied to the solution containing gelatin with the error of about ±2% in our experiment.

Measurement of Viscosity.—The viscosity of the mixed solutions was measured by means of a horizontal capillary tube viscosimeter, the solution having been made to flow through the tube under suitable pressure differences at the two ends of the tube. The pressure difference was maintained constant during a set of measurements by means of a manostat. The radius of the capillary tube was equal to 0.031 cm. and its length 30.3 cm. The pressure range studied was from 0.5 cm. to 11 cm. in mercury manometer.

Results and Discussion

a) Complex formation.—Various amounts of detergents were added to a 0.5% gelatin solution at various values of pH of the solution, which had been controlled by adding normal HCl or NaOH to the solution. It was found that gelatin was precipitated in a certain range of the concentration of any one of the detergents at a certain value of pH of the solution. DAH precipitated gelatin at pH values greater than that of the isoionic point, while SDS precipitated gelatin at pH values less than that of the isoionic point. When precipitates appeared, the resulting mixture, after being allowed to stand for twenty four hours, was centrifuged or filtered, and the concentration of detergent of the supernatant or filtered solution was determined as described above; the amount of detergent combined with the precipitant was thus obtained by taking the difference of concentration which existed before and after the process. Figs. 1a. and 1b. show the amount of the combined detergent in relation to the ratio of detergent to protein.

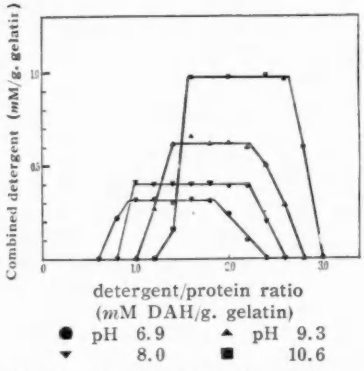


Fig. 1a. Amount of combined detergent (DAH) in relation to detergent/protein ratio.

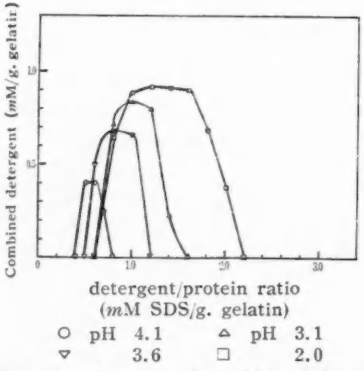
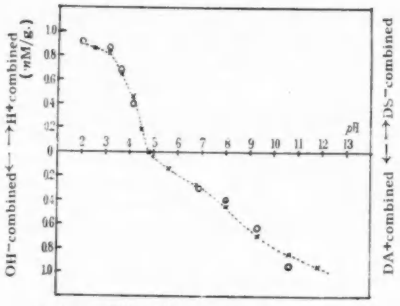


Fig. 1b. Amount of combined detergent (SDS) in relation to detergent/protein ratio.

As these figures indicate, the precipitation zone is greatly influenced by the pH of the mixed solution and, in the case of gelatin-dodecyl amine ion combination, the precipitation zone is displaced to the higher ratio of detergent to protein as pH becomes greater, while in the case of gelatin-dodecyl sulphate ion combination, the precipitation zone is displaced to the higher ratio of detergent to protein as pH becomes smaller. In both cases, it is to be remarked that the maximum precipitation and the complete dissolution of the precipitate take place at the definite ratio of the detergent concentrations, namely 1:2. It is also noticeable that SDS precipitates gelatin at much lower concentrations than DAH does.

10) T. Ino, T. Kondo, K. Meguro and O. Yoda, *J. Chem. Soc. Japan*, **76**, 220 (1955).



×···×··· Titration curve
○ Maximum value of combined detergent.

Fig. 2. Titration curve of gelatin and maximum value of combined detergent at each pH.

Fig. 2 shows that the maximum values of detergent combined at each pH are approximately corresponding to the acid or base combining power of gelatin, and therefore it is concluded that the first polar combination between gelatin molecules and detergent ions is accomplished at the point of the maximum precipitation.

b) Flow Properties.—The flow of gelatin solutions in presence and absence of detergent was found generally non-Newtonian, the rate of flow being expressed by the well known Bingham's equation[11], namely:

$$\frac{V}{t}=\frac{\pi\mu R^4}{8l}\left(P-\frac{4}{3}p+\frac{p^4}{3P^3}\right),$$

where, V means the volume of the solution passed through the capillary tube in time t, R the radius of the capillary tube, l the length of the tube, P the difference of pressures applied, μ the coefficient of mobility, p a constant equal to $\frac{2l}{R}f$ in which f means the yield value. When the applied pressure difference is large, the curve V/t *vs.* P becomes nearly linear, and it obeys the following equation:

$$\frac{V}{t}=\frac{\pi\mu R^4}{8l}\left(P-\frac{4}{3}p\right)$$

Putting herein $V/t=0$, we obtain the intercept at the axis P and from this we get the value of the yield value. From the slope of the asymptote we obtain the value of $\frac{\pi\mu R^4}{8l}$ and consequently the value of the coefficient of mobility $\mu:\mu=1/\eta$, where η means the coefficient of viscosity. In this paper, we conventionally use the relative viscosity to water, η_r, instead of μ or η.

The relative viscosity and the yield value obtained of the gelatin solution first in absence of detergent are shown in Fig. 3, both as a function of pH. As this figure demonstrates, η_r and f run completely parallel to each other. Both the values have the minimum at the isoionic point and the maximum on both sides of the isoionic point. Such a characteristic feature was formerly found by Freundlich and Neu kircher[12] and recently studied in some detail by Stainsby[13].

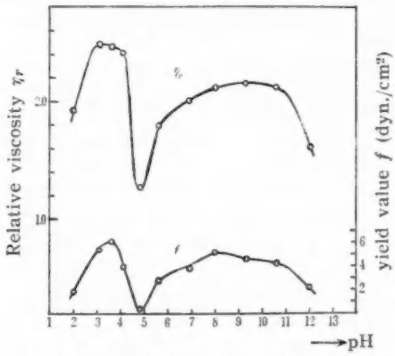
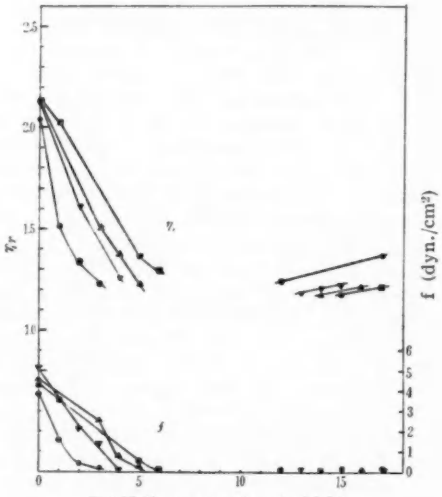


Fig. 3. Viscosity and yield value of gelatin solution as a function of pH. Solution: 0.5%, Temperature: 25°C.



● pH 6.9 ▼ pH 8.0 ▲ pH 9.3 ■ pH 10.6

Fig. 4a. Variation of viscocity and yield value of gelatin solution by addition of DAH. Solution: 0.5%, Temperature: 25°C.

11) E.C. Bingham, "Plasticity and Fluidity" New York, (1922) p. 222.

12) H. Freundlich and H. Neukircher, *Kolloid-Z.*, **38**, 180 (1926).

13) G. Stainsby, *Nature*, **169**, 662 (1952).

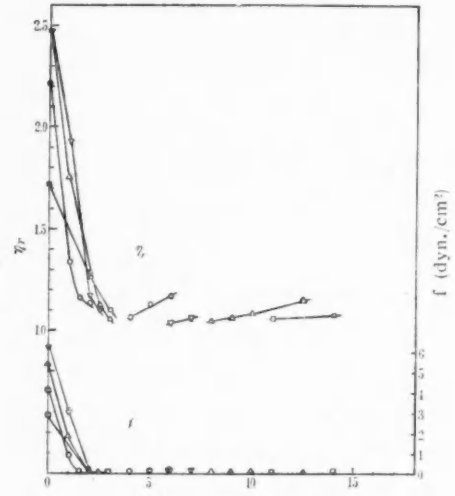


Fig. 4b. Variation of viscosity and yield value of gelatin solution by addition of SDS. Solution: 0.5%, Temperature: 25°C.

At the isoionic point, the macromolecule of gelatin is probably in the contracted form owing to the attractive forces between balanced charges, whereas, on both sides of the isoionic point, the molecule has a net charge, which may cause it to extend itself by repulsion. However, in more acidic or more basic solutions, the repulsive forces will be again reduced, owing to the increase of free ions in those solutions. The maximum of η_r and f on both sides of the isoionic point may be the result of the interplay of these two counter effects.

Fig. 4a shows how η_r and f of the solution change by the addition of DAH within certain range of detergent concentrations either before the precipitation or after the redissolution. Fig. 4b shows the similar change of η_r and f in the case of gelatin-SDS mixtures. In both cases, we find such a tendency that the values of η_r and f are greatly reduced as detergent is added until precipitation takes place and that, after redissolution of the precipitate initially formed, the mixture exhibits nearly Newtonian flow. The mechanism of the phenomena may be considered as follows. The more or less expanded gelatin molecule either at the acidic or alkaline side of the isoionic point may be changed into the folded, hydrophobic state by the continuous combination of detergent ions and consequently η_r and f decrease until precipitation takes place. On addition of excess detergent, however, the second adsorption layer of detergent ions will be formed by van der Waals attraction force between carbon chains, which makes the molecule hydrophilic and accordingly the precipitate once formed dissolves again into solution. The solution thus formed behaves itself similarly to the solution at the isoionic point without detergent.

It is remarkable that the relative viscosity of the mixed solutions, directly before the precipitate formation or directly after the dissolution of the precipitate, is somewhat less than that of the solution at the isoionic point. This suggests that the gelatin molecule in such mixtures may be in more folded state than the molecule at the isoionic point. It is further noticed from our experiment that SDS reduces the viscosity of the gelatin solution more effectively than DAH does and consequently that SDS is more effective than DAH in precipitating gelatin from the solution. This agrees with the general character of proteins that they interact more strongly with anions than with cations.

Furthermore, the combination of detergent ions with cationic or anionic groups of the macromolecules of gelatin would have taken place mainly at the side chains and probably not at the backbone in the case of our experiment, because the interaction was studied in absence of any other inorganic salts except that very small amount of sodium chloride formed by the neutralization of detergent ion with HCl or NaOH.

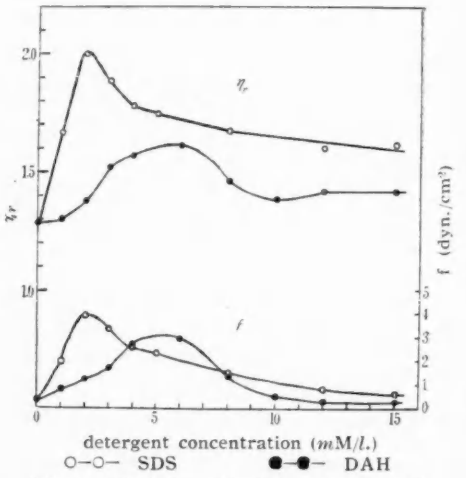


Fig. 5. Variation of viscocity and yield value of gelatin solution by addition of detergent at isoionic point. Solution: 0.5%, Temperature: 25°C.

Lastly, Fig. 5 indicates the change of η_r and f of the mixture in relation to the added DAH or SDS at the isoionic point of gelatin. As this figure shows, both η_r and f increase first with the addition of detergent, attain maxima and then decrease. Comparing these curves of η_r or f in this figure with those in Fig. 3, which show the change of η_r or f due to the addition of hydrogen ion or hydroxy ion to isoionic gelatin, we find a remarkable resemblance in the features of the corresponding curves. This suggests that the effect of detergent cations or anions upon gelatin bears a resemblance to that of hydrogen ion or hydroxy ion upon the same gelatin. It is thus quite presumable that either detergent cations or anions combine with a neutral gelatin molecule to some extent to give it net charges and consequently cause the molecule to extend itself. The appearance of maximum and decrease of η_r or f with increasing detergent concentration is probably due to the screening effect of counter ions.

Summary

The action of dodecyl amine hydrochloride and sodium dodecyl sulphate on gelatin was studied at various hydrogen ion concentrations of the mixed solution, once by determining the combined detergent ions to the precipitated gelatin and then measuring flow properties of mixed solutions.

The determination of the combined detergent ions showed that the complex formation between detergent and gelatin should have taken place according to the mechanism proposed by Pankhurst and his co-workers.

The non-Newtonian flow character of gelatin solution at pHs on both sides of the isoionic point, was greatly influenced by the addition of detergent cations or anions and the flow of the mixed solutions directly before the precipitate formation or after the precipitate dissolution became approximately Newtonian, which suggested that the gelatin molecule would have been brought into a more folded state by the successive combinations of detergent ions.

The viscosity coefficient as well as yield value of the gelatin solution at the isoionic point were found to increase by the addition of detergent cations or anions. This suggested that the folded isoionic gelatin molecule would have been expanded by the combination with either one of the detergent ions.

We should like to express our sincere thanks to Armour and Co. U. S. A. and Nezu Chemical Laboratory, Tokyo, for their kind supply of pure detergents.

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Chemistry Department, College of General Education; and Institute of Science and Technology, The University of Tokyo, Tokyo

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The Crystallinity of Solid High Polymers. I. The Crystallinity of Polyvinyl Alcohol Film[*1]

By Hiroyuki TADOKORO, Syûzô SEKI and Isamu NITTA

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Introduction

The recent studies on solid high polymers have emphasized that the crystallinity is one of the most important factors to describe the state of them. The crystallinity is generally defined as the weight fraction of crystalline material. This definition is quite distinct if the polymer material is made of two distinct parts perfectly crystalline and perfectly amorphous. However, it is possible that there exist a transitional intermediate zone between these two perfect regions. In fact the same chain molecule may pass continuously from the one to the other region several times through such an intermediate zone. From this point of view the term "crystallinity" will be by nature an approximate one. During the past decade various methods of estimating crystallinity have been devised and developed, such as

[*1] This paper was read at the discussion meeting on the high polymers under the auspices of the Kinki Branch of the Chemical Society of Japan and the Kansai Branch of the Society of Polymer Science (Japan) held in Kyoto on 9, Nov. 1954.

X-ray diffraction[1,2], density[3,4], infrared absorption spectrum[2,5], specific heat[6] etc. On the other hand some authors determine as a measure of this quantity the so-called "accessibility" by making use of the isotope exchange[7], hydrolysis[8] or sorption of water vapor[9,10]. In view of the conceptional limit of crystallinity mentioned above as well as the variety of detailed texture of polycrystalline high polymers, such as distribution of the size and shape of crystallites, their orientation, etc., it becomes of great importance to examine these methods of estimating crystallinity more critically as to what characteristic each of them possesses.

Although there exist a considerable number of reports on the crystallinity for cellulose[1a,3,7,8,9,10], polyethylene[1b,2,4,5a,6a,6b] nylon[2,5c,10], polyethylene terephthalate[2,5] etc., little work has been done with the same samples prepared under the same conditions by the comparative use of various kinds of existing methods estimating the crystallinity. In order to make some contribution to such a problem, we have undertaken to clarify the relationship among density, sorptive power for water vapor and infrared absorption spectrum as the proposed measures of the crystallinity, using the samples of polyvinyl alcohol (PVA) subjected to heat-treatments at different temperatures, each of which was prepared from one and the same source of material.

1a) P.H. Hermans and A. Weidinger, *J. Appl. Phys.*, **19**, 491 (1948); idem., *J. Polymer Sci.*, **4**, 135 (1949). b) S. Krimm and A.V. Tobolsky, *J. Polymer Sci.*, **7**, 57 (1951).

2) J.B. Nichols, *J. Appl. Phys.*, **25**, 840 (1954). (Review about the X-ray and infrared spectroscopic method).

3) P. H. Hermans, *J. Polymer Sci.*, **1**, 162 (1946); idem., "Contribution to the Physics of Cellulose Fibers", Elsevier Publishing Co., Inc., Amsterdam—New York, (1946), p. 70; "Physics and Chemistry of Cellulose Fibers", same publisher, (1949), p. 205.

4) E. Hunter and W.G. Oakes, *Trans. Faraday Soc.*, **41**, 49 (1945).

5a) R.B. Richards, *J. Appl. Chem.*, **1**, 370 (1951). b) W.H. Cobbs, Jr., and R.L. Burton, *J. Polymer Sci.*, **10**, 275 (1953). c) G.B.B.M. Sutherland and A. V. Jones, *Discussions Faraday Soc.*, **9**, 281 (1950). d) J.T. Maynard and M.B. Hall, *J. Polymer Sci.*, **12**, 235 (1954). Even in the case of ionic crystals this method can reveal the difference of the states of aggregation which cannot be differentiated by the X-ray method. (G. Chaudron, H. Mondange and M. Pruna, *Proc. Inter.n. Symposium Reactivity of Solids, Gothenburg* (1952) 9. *Chem. Abst.*, **48**, 13314a (1954).).

6a) H.C. Raine, R.B. Richards and H. Ryder, *Trans. Faraday Soc.*, **41**, 56 (1944). b) M. Dole, W.P. Hettinger, Jr., N.R. Larson and J.A. Wethington, Jr., *J. Chem. Phys.*, **20**, 781 (1952). c) R.C. Wilhoit and M. Dole, *J. Phys. Chem.*, **57**, 14 (1953). d) J.D. Hoffman, *J. Am. Chem. Soc.*, **74**, 1696 (1952).

7) V.J. Frilette, J. Hanle and H. Mark, *J. Am. Chem. Soc.*, **70**, 1107 (1948).

8) H. Maeda, *Chem. and Engineering (Japan)*, **4**, 429 (1951). (Review of the chemical methods).

9) J.A. Howsmon, *Text. Res. J.*, **19**, 152 (1949).

10) A.J. Hailwood and S. Horrobin, *Trans. Faraday Soc.*, **42B**, 84 (1946).

Experimental

a) Sample.—The powdered specimen of PVA (average degree of polymerization: 1650) was used as a starting material. The method of purification of the sample and the procedure adopted for the preparation of film specimens were the same as those described already in the previous paper[11]. Several large films prepared were all 0.01–0.03 mm. thick and they were cut in pieces of about 5 mm. × 10 mm. These small pieces of films were then divided into four groups, and each group was placed on a paper in an air-thermostat and subjected to the heat-treatments, the conditions of which are given in Table I. A part

TABLE I

Sample	Conditions of heat-treatments	Appearance
I	No heat-treatment	———
II	100°C, 30 min.	Almost no change
III	160°C, 15 min.	
IV	193°C, 2.5 min.	Colored slightly brownish

of the specimens of each group mentioned above were then cut further in smaller sizes of about 1 mm. × 5 mm. and they were used for the density measurements.

b) Apparatus and Procedures.—The sorption and desorption*2 isotherms were measured by the desiccator method and the measurements of the density were carried out by the flotation method. The apparatus and the procedures are essentially the same as before[11], so the description of them may be omitted here. The drying condition was about 60°C under a high vacuum (10^{-4} mmHg or below) over phosphorous pentoxide, the vessel being connected to a liquid air trap. For the attainment of constant weight it took about five days. The experiments of sorption and desorption as well as the measurements of density were all performed at 25° ± 0.03°C. For the sorption equilibrium it required about three weeks.

Infrared (from 2 μ to 15 μ) and ultraviolet absorption spectra (from 200 mμ to 550 mμ) were also taken for reference to those experiments mentioned above, by using the Perkin-Elmer Model 21 Double Beam Recording Infrared Spectrophotometer with sodium chloride prism and the Beckman Model DU Quartz Spectrophotometer with ultraviolet accessaries respectively.

Results and Discussion

a) Density.—The densities of the bone-dry samples at 25°C are given in Table II. They seem to increase with the rise of the temperatures of heat-treatments. In order to evaluate the crystallinity of a sample from the density data, it is necessary to know the densities of crystalline as well as amorphous

11) H. Tadokoro, S. Seki and I. Nitta, This Bulletin, **27**, 451 (1954).

*2 The details of our desorption experiments will be reported in the next paper.

TABLE II

Sample	Density at 25°C. (g./cc.)	Crystallinity (From density and X-ray data)	$R/44$
I	1.291_0	0.29	5.7
II	1.294_5	0.34	5.9
III	1.300_7	0.42	5.9
IV	1.306_6	0.49	4.7

regions. The density of the former was calculated to be about 1.34 g./cc. from the lattice constants determined by X-ray investigation[12-15]. On the other hand, that of the latter cannot be measured directly, since the preparation of completely amorphous PVA has not yet been successful. By assuming that the ratio of the density of the amorphous to that of the crystalline state for PVA is of the same order of magnitude as that for other organic hydroxyl compounds, such as butyl alcohol (0.94)[16], as P. H. Hermans did in the case of cellulose[3], the density of the amorphous part was estimated to be about 1.26 g./cc. Recently I. Sakurada and his coworkers found that the crystallinity estimated by the X-ray method for the PVA film specimens, prepared under various conditions of heat- and stretching-treatments, shows an approximately linear relationship with their densities[17]. By extrapolation to zero for the crystallinity they found the density of the amorphous part of PVA to be 1.27 g./cc. This value coincides with that derived above by Hermans' method within experimental error. By use of the density values for the four groups of the specimens in column 2 of Table II together with the relationship of Sakurada et al., we can thus calculate their crystallinity, which is shown in column 3 of the same Table.

We measured also the densities of the samples at moist states for reference. As shown in Fig. 1, each density curve showed a conspicuous maximum at about 1.7, 1.5, 1.1 and 0.8% water content for the samples I, II, III and IV, respectively. This tendency is in good agreement with the discussion in the previous paper which indicated that the

b) Sorption of water vapor.—The sorption isotherms of water vapor by the PVA films are all given in Fig. 2 and Table III.

As is well known, there are two methods

12) R.C.L. Mooney, *J. Am. Chem. Soc.*, **63**, 2828 (1941).
13) C.W. Bunn and H.S. Peiser, *Nature*, **159**, 161 (1947); C.W. Bunn, ibid., **161**, 929 (1948).
14) I. Sakurada and K. Fuchino, *X-Rays*, **6**, 66 (1950); *Rep. Sci. Res. Inst. (Tokyo)*, **20**, 890 (1941).
15) I. Nitta and I. Taguchi, *Ann. Report Inst. Fiber Res. (Osaka Univ.)* **6**, 3 (1952).
16) W. Biltz, *Z. physik. Chem.*, **A151**, 13 (1930).
17) I. Sakurada, Y. Sone and Y. Nukushina, Annual Meeting of the Chem. Soc. of Japan in April 1954.

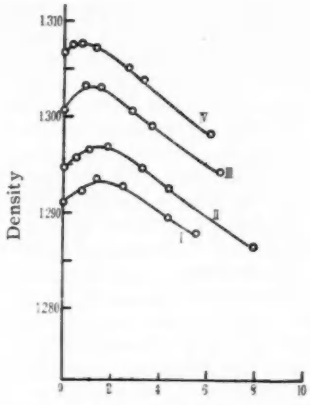


Fig. 1. Density-water content curves.

water content at which the density shows maximum, decreases in the reverse order to the crystallinity[11].

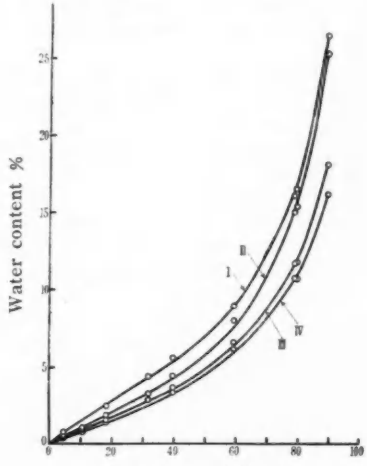


Fig. 2. Sorption isotherms at 25°C.
∘ Observed value
— Calculated value

TABLE III

Relative humidity	Water content I	II	III	IV
0.048	0.0079	0.0052	0.0046	0.0036
0.108	—	0.0107	0.0088	0.0075
0.184	0.0247	0.0182	0.0153	0.0132
0.318	0.0431	0.0323	0.0282	—
0.396	0.0553	0.0436	0.0364	0.0330
0.594	0.0890	0.0796	0.0652	0.0610
0.790	0.1606	0.1500	0.1165	0.1070
0.797	0.1650	0.1537	0.1175	0.1067
0.897	0.2640	0.2521	0.1807	0.1617

of estimating the crystallinity of polymers, in a relative sense, from the sorption data: i) the sorption ratio method[9] and ii) the Hailwood-Horrobin method[10].

i) Sorption ratio method.[9]—Sorption ratio means the ratio of the water content of a sample to that of a standard sample at the same relative humidity. This ratio is thought to be proportional, in a rough sense, to the fraction of the amorphous region. In the present experiment, sample I was arbitrarily taken as the standard, whereas native cotton has been usually taken as the standard in the case of cellulose.

As for the relative humidity we selected 59.4%, where the swelling is not yet perceptible and the accuracy of the observed data is rather high. Fig. 3 shows the relation between the sorption ratio at this relative humidity and the density.

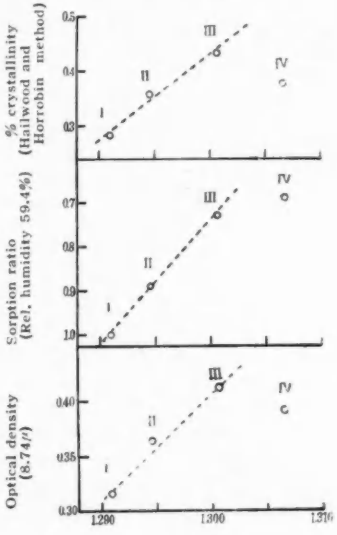


Fig. 3. Crystallinity-density curves (by water sorption and infrared absorption spectrum).

ii) The Hailwood-Horrobin method.[10]—Hailwood and Horrobin postulated that moist high polymer is an ideal solid solution of dissolved water, unhydrated polymer molecules, and hydrated polymer molecules, assuming:

$$\frac{W_i}{W_{i-1}a'}=K_i \qquad i=1,\ 2,\ \ldots\ldots \tag{1}$$

where a' is the activity of the dissolved water in the soild phase, W_i is the activity of the i-th hydrate of the polymer, and K_i is the appropriate equilibrium constant. It follows that:

$$W_i=W_0(a')^iK_1K_2\ldots\ldots K_i \tag{2}$$

where W_0 is the activity of the unhydrated polymer. Using:

$$a'=\bar{K}x \tag{3}$$

where x is the activity of the water in the vapor phase and $\bar{K}$ is a constant, they then equate the activities of the various species to their mole fractions assuming the formation of an ideal solution. This leads them to the following three-parameter equation, neglecting the second and higher hydrates,

$$\frac{Mr}{1800}=\frac{\bar{K}h}{1-\bar{K}h}+\frac{\bar{K}K_1h}{1+\bar{K}K_1h} \tag{4}$$

where M is the "molecular weight" of the operative polymer unit, r is the regain, i.e. the total grams of water absorbed per 100 grams of bone-dry polymer, and h is the relative humidity. Further (4) can be put into the following form:

$$A+Bh-Ch^2=h/r \tag{5}$$

All the curves shown in Fig. 2 were drawn by using three parameters A, B and C which were calculated from the data of Table III by the method of least squares. We could find that this equation fit the observed values well.

Assuming that water molecule is not accessible to the interior of the crystalline region, Hailwood and Horrobin then correlated the constant M in this equation (4) with the accessible fraction θ by the following relation:

$$M\theta=R \tag{6}$$

where R ($\leq M$) is the molecular weight of the "unit" of the polymer molecule which is capable of combining with one molecule of water to form a monohydrate and is equal to M when the polymer is completely amorphous. They assumed further that the value of R is equal to the molecular weight of the unit which contains one characteristic polar group. In our previous paper[11], we assumed that the monohydrate consists of one polymer unit -(CH_2CHOH)- and one water molecule according to the method of Hailwood and Horrobin. However, since the value of R cannot be checked as such from the measurement of water sorption only, the crystallinity on the basis of the assumed R would be used at most only as a relative measure. In order to see if the value of R comes out to be corresponding to the monomer unit, we calculated it by utilizing the crystallinity shown in column 3 in Table II and the value of M obtained from A, B and C. In column 4 of Table II, are shown the values of $R/44$ which correspond to the

number of monomer units per one monohydrate (molecular weight of monomer unit =44). It is rather remarkable that these values for samples I, II and III are nearly constant (5.7–5.9) in spite of the rather naïve and crude theoretical treatment by Hailwood and Horrobin, and at the same time the value for sample IV (4.7) is considerably different from the other three, being parallel to the experimental evidences of sorption ratio and others which will be mentioned below. These results will show that this method may be utilized for estimating the relative crystallinity of this material. However, the questions why these values come out nearly constant and whether their magnitude has a definite physical meaning or not, might be solved first by further experiments; the measurement of the adsorption at very low humidity may be useful in this respect.

By taking $R/44=5.8$ for all samples, the crystallinities are then calculated and plotted against the density in Fig. 3.

c) **Infrared absorption spectrum.**—Fig. 4 shows a part of the infrared absorption spectra of our samples. The curve covering the whole region in this figure is for sample I, while for the other samples only the absorption band at 8.74μ(1146 cm^{-1}) is given by adjusting the intensity of absorption of seven other bands (3.4μ, 7.0μ, 7.40μ, 8.06μ, 9.15μ, 10.9μ and 11.75μ) to fit with those of sample I. Although the optical density of the broad and very strong 3.0μ band changes sensitively with the amount of bound water as some investigators reported[18,19], we have confirmed that those of the above-mentioned seven bonds do not depend on the water content. We have also found that the intensity of the 8.74μ band is not affected by the bound water so long as the water content does not exceed several percent. According to the investigation by A. Elliott et al., this band shows striking effect of dichroism, and they also inferred that this band may be due to a kind of absorption mechanism relating to the presence of the oxygen atoms[20]*3. Recently, E. Nagai and his coworkers found further that this band becomes stronger and stronger as the heat-treatment proceeds until the sample becomes colored[21]. As shown in Fig. 4, the intensity of absorption of this band increases in the order of samples I, II and III, and then decreases in IV. The optical density of this band vs. the density is given in Fig. 3. By the linear relationship of the intensity variation of this absorption band to the density and also by other facts mentioned above, we confirmed that this band is really the so-called "crystallization-sensitive" band[2].

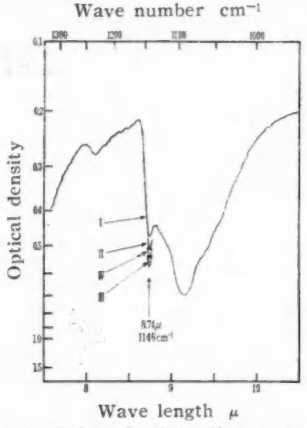


Fig. 4. Infrared absorption spectra of PVA films.

Now we proceed to the relationship among these results obtained above. In Fig. 3 the values given in ordinates for the samples I, II and III lie nearly on straight lines, whereas remarkable deviations are found for the sample IV. As the sample IV was subjected to the heat-treatment at the highest temperature, and got colored considerably, so it may be conceived that such an abnormality is due to the occurrence of some chemical changes.

In order to ascertain whether it is really the case or not, the ultraviolet absorption spectra were measured. Our results are shown in Fig. 5, in which the absorption bands at 280 mμ and 330 mμ are particulary distinguished for the sample IV. These two bands are considered to be attributed to carbonyl group and carbon-carbon double bond conjugated with the carbonyl group respectively. This conclusion is also in agreement with the results obtained by J. Ukita and his coworkers using the chemical method[22]. As the occurrence of chemical changes in

18) H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **41**, 246 (1945).

19) L. Glatt, D.S. Webber, C. Seaman and J.W. Ellis. *J. Chem. Phys.*, **18**, 413 (1950).

20) A. Elliott, E.J. Ambrose and R.B. Temple, *J. Chem. Phys.*, **16**, 877 (1948).

*3 The elucidation of the origin of this band seems to have considerable significance for clarifying the nature and structure of the crystalline part. To get further information we are now studying this point by means of deuterium exchange (H. Tadokoro, S. Seki and I. Nitta, *J. Chem. Phys.*, **23**, 1351 (1955)).

21) E. Nagai, S. Mima, S. Kuribayashi and N. Sagane, *Chem. High Polymers (Japan)*, **12**, 199 (1955).

22) J. Ukita, S. Usami and T. Kominami, *Chem. High Polymers (Japan)*, **11**, 300 (1954).

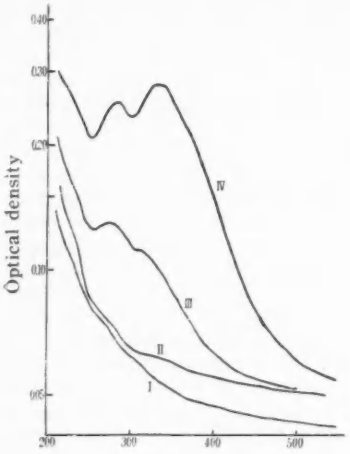


Fig. 5. Ultraviolet absorption spectra of PVA films.

the sample IV were thus ascertained, it may be of less significance to discuss the crystallinity of this sample in comparison with the other three samples on the same grounds. In passing, it may be added here that we found recently the fact that when the heat-treatment was carried out above the temperature of about 180°C, the density-time curve at constant temperature for such a sample shows a maximum in contrast to those treated at lower temperatures*4. This fact may also be explained by the occurrence of chemical changes.

After all, it is ascertained in the present investigation that the crystallinity measured by the X-ray, density, water sorption and infrared absorption methods go approximately parallel with each other as far as chemical change on heating is not appreciable, so the methods we have adopted in the present work may be used for determining the crystallinity.

Although we can correlate the four above-mentioned methods estimating the crystallinity with each other, it would be necessary to carry out further investigation in relation to the detailed texture of solid high polymers in order to obtain deeper insight into the nature of this quantity, "crystallinity". From such a standpoint, we are led to investigate such problems as given below and examine the results with systematical and synthetical criticism:

i) the application of the method for measuring the accessibility, e. g. deuterium exchange*3,

ii) the application of the method for studying the texture, e. g. X-ray small angle scattering*5,

iii) the assignment of the crystallization-sensitive band in infrared absorption spectra*3,

iv) the application of a new method for localizing hydrogen atoms, e. g. proton magnetic resonance absorption, chemical shift,

v) the comparative investigations with other high polymers, e. g. cellulose, nylon, etc.

*4 Details of this experiment will be published later.

Summary

i) Densities, sorption of water vapor and infrared absorption spectra were measured on four kinds of PVA films, which were prepared from the same PVA powder specimen and subjected to different heat-treatments.

ii) It was found by the present investigation that the 1146 cm^{-1} (8.74μ) band is the so-called crystallization-sensitive band.

iii) Since the degrees of crystallinity determined by these methods went in parallel, it was found that they may be used as relative measures for the crystallinity.

iv) Samples subjected to the heat-treatment at about 193°C, behave abnormally from the other three groups of samples. This deviation was found to be due to chemical changes occurring in the heat-treatment. This was confirmed by the measurement of ultraviolet absorption spectra.

The authors express their sincere thanks to Mr. Y. Sone of the Institute for Chemical Research of Kyoto University for helpful advice and criticism, to Messrs. E. Nagai and S. Kuribayashi of the Osaka Industrial Research Institute and Dr. M. Momotani of Momotani Juntenkan Co., Ltd. for preparing charts of infrared absorption spectra, to Mr. S. Fukushima of this Faculty for preparing data of ultraviolet absorption spectra, to Mr. K. Kôzai for his collaboration in our experiments, and to Kurashiki Rayon Co., Ltd. for kindly giving them the PVA samples.

Department of Chemistry, Faculty of Science, Osaka University, Osaka

*5 For the elucidation of the texture, the X-ray small angle scattering method seems to be very helpful. For this purpose Dr. M. Kakudo of the Faculty of Engineering of this University is now studying this problem in relation the to same materials we are using at present in accordance with our request.

Note added in Proof: According to Fig. 1 of the paper by E. Nagai, S. Mima, S. Kuribayashi and N. Sagane[3]) the fourth point (of the specimen of the density 1.306e) lies on the straight line. This is in contradiction to our result. Such discrepancy might be due to the fact that they have chosen 3.0 μ absorption band as the standard, which does not seem to be adequate judging from our observation.

*Studies on Several Phosphates from the View-point of Analytical Chemistry. IV. A Radioactive Paper Chromatography on Several Meta- and Poly-Phosphates labelled with P^{32}**

By Mutsuaki SHINAGAWA, Junichi TAKANAKA, Yoshiyuki KISO, Aiko TSUKIJI and Yōko MATAMA

(Received November 15, 1954)

Recently the studies on several meta- and poly- phosphoric acids and their phosphates have been carried on by many investigators, but it appears that no definite method for separational analysis has been yet established. Therefore, the authors synthesized several phosphates labelled with P^{32} and investigated their chromatograms at various rates using pyridine-water as solvent.

Material and Reagents

(1) Samples

Samples were obtained by synthesizing sodium ortho-, pyro-, tripoly-, trimeta- and hexametaphosphates, each labelled with P^{32}.

As there was only a little radioactive material, it was impossible to synthesize the labelled substances to a great degree. Hence we were unable to use it as a purified sample.

a) Disodium-hydrogen-orthophosphate (Na_2HPO_4)[1]. —With reference to Richard C. Vogel and H. Podall's report[1], the preparation was made by adding 10 ml. of "carrier-free" phosphate (by diluting 2 mc. of "carrier-free" to 50 ml. of distilled water slightly acidified by hydrochloric acid) to 1 g. of disodium-hydrogen-orthophosphate. After agitation at 110°C it was used as a dehydrated salt.

b) Sodium-pyrophosphate ($Na_4P_2O_7$)[2].—About 1 g. of sodium-dihydrogen-orthophosphate was heated in a platinum-crucible and maintained at 210°C for twelve hours. The purity was more than 97%.

c) Sodium-trimetaphosphate ($Na_3P_3O_9$)[2].—About 1 g. of sodium-dihydrogen-orthophosphate was heated in a platinum-crucible and maintained at 300°C for one hour and then at 610°C for three hours, lowered to 390°C slowly in that same condition, and then allowed to stand for fourteen hours. After the finely powdered substance was placed in a desiccator, this was lowered to room temperature.

d) Sodium-tripolyphosphate ($Na_5P_3O_{10}$)[2].—Sodium-dihydrogen-orthophosphate and disodium-hydrogen-orthophosphate were mixed in the proportion of 1:2. This was heated to 800°C and maintained at this temperature for a period of eighteen hours, so it could completely melt. The temperature was then lowered gradually from 650°C to 250°C, which required about eight hours, and then cooled in a desiccator.

e) Sodium-hexametaphosphate ($Na_3P_3O_{18}$)[2].—Monosodium-dihydrogen-orthophosphate was heated to about 900°C and maintained at this temperature for three hours in a platinum crucible and then the melted mass was cooled rapidly. Different batches of the resulting glassy product contained from 90% to 95% sodium-hexametaphosphate.

Each phosphate was dissolved in water and about 0.1 mol. solutions were prepared.

(2) Solvents

The solvents were prepared by mixing *n*-C_4H_9OH, and H_2O and 11 N NH_4OH in the ratio of 8:1:1 in volume respectively and by mixing pyridine and water in the ratios of 0:1, 1:4, 3:7, 1:2, 2:3, 1:1, 3:2, and 1:0 in volume.

(3) The Method of Development

The chromatograms were developed by the ascending method on Toyo Rosi No. 50 paper for six to ten hours in a chromatographic cylinder, which was kept at 25±1°C in the thermostat. The making of the cylinder was based on W. H. Longenecker[3] and Otosai's apparatus[4]: The size of paper was 1 cm.×40 cm. and sufficiently long to provide a chromatograph path of 30 cm. On this about 0.02 micro-mol. of samples were placed with capillary on each sheet approximately 4 cm. above the surface of the solvent.

(4) The Method for Detection

Recently studies on application of chromatography by using the radioactive method were made by H. Muller[5] and H. H. Strain[6], who also devised a convenient apparatus for measuring radiation. The authors devised a simple apparatus, which was used in the test as shown in Fig. 1.

The following were used in this apparatus.

Hundred scaling G. M. Counter (Kobe Tech. Co.).

Two sheets of stainless steel (10 cm.×10 cm.×2 mm.) for slit.

A glass plate (10 cm.×30 cm.×2 mm.) upon which the papers were slid. A 30 cm. ruler.

* Presented at the 7th. Annual Meeting of Chem. Soc. of Japan, April 1954.

1) R.C. Vogel and H. Podall, *J. Am. Chem. Soc.*, **72**, 1420 (1950).

2) L.T. Jones, *Ind. Eng. Chem. Anal. Ed.*, **14**, 536 (1942).

3) W.H. Longenecker, *Anal. Chem.*, **11**, 402 (1949).

4) K. Otosai, *Kagaku no Ryoiki*, **8**, No. 8, 25 (1950).

5) R.H. Muller, *Anal. Chem.*, **23**, 208 (1951).

6) T.R. Sato, W.P. Norris and H.H. Strain, *Anal. Chem.*, **24**, 776 (1952).

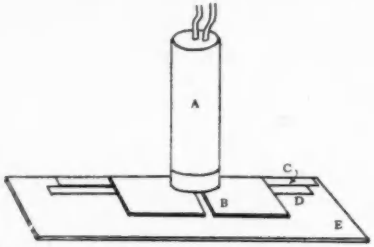


Fig. 1. Counting technique. A, counter tube holder; B, stainless steel slit; C, 30 cm. ruler; D, paper; E, glass-plate.

As shown in Fig. 1 the position of the G. M. tube is fixed. Two sheets of stainless steel were used to make a slit, the width of which was adjustable from 0.25 to 0.5 cm. These steel plates were placed over the glass plate, between which the paper could be moved at intervals of 0.25 or 0.5 cm. At each interval the count was made for one minute. The measured counting rates per minute were plotted against the developed distances.

During the measurement, there was no possibility of contamination on the surface of the slit or elsewhere. This was proved from the results of various tests.

Rf's were determined from the positions which are shown as the maximum counting rate.

Several phosphate ions came to their characteristic places regularly in the paper according to the differences of mobilities.

Results and Discussion

a) Although the separation of several phosphate ions was examined with the solvent of n-$C_4H_9OH-H_2O-11$ N NH_4OH (8 : 1 : 1), the result was not successful. Rf's were approximately zero.

b) The developed states of a crude hexameta-phosphate at the various rates of pyridine-water solvent are shown in Fig. 2, in which the greatest peak should be hexametaphosphate, the main component, while others having the smaller peaks should be some impurities of the other types of phosphates.

From Fig. 2 it could easily be recognized that the most satisfactory result was obtained in the case of pyridine-water (1 : 1) and the result was found to be reproducible. Fig. 3 was introduced from the relation of Rf's of several phosphates ions with the various rates of pyridine-water solvent.

The results showed the following. When samples were developed only with water, all Rf's were nearly 1.0, but trimetaphosphate ions could be separated a little from other ions. Consequently, the other mutual ions except trimeta-ion could not be separated completely.

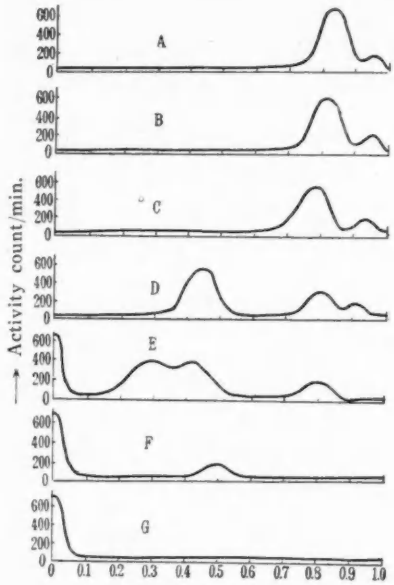


Fig. 2. Radioactive chromatograms of synthesized hexametaphosphate at various rate of pyridine-water.

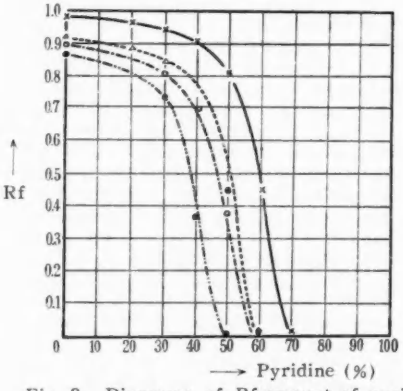


Fig. 3. Diagrams of Rf-amount of pyridine (%). △, orthophosphate ion; ⊙, pyrophosphate ion; ×, trimetaphosphate ion; ○, tripolyphosphate ion; ●, hexametaphosphate ion.

Corresponding to the increase of pyridine the mutual separation among several phosphate ions gradually became possible. Pyridine-water (1 : 1) appeared to be the most desirable solvent for separation.

When the rate of pyridine was increased further, Rf's of each phosphate ion decreased and approached zero. However, the decrease of trimeta ions was comparatively delayed.

A in Fig. 4 shows the peak of trimeta-

phosphate ion. B in Fig. 5 shows the case in which hydrolysis of hexametaphosphate did not occur. The small peak at the right hand side in the figure indicates an impurity of the hexametaphosphate. This can be quite conceivable from the results of the other investigators[7]. C in Fig. 4 shows the result of the tripolyphosphate ion having a indistinct double peak. The peak having smaller Rf-value was due to tripolyphosphate ion and the other was due to orthophosphate ion, according to the peak shown in G in Fig. 4 which was due to orthophosphate ion. A peak of similar nature can be seen in D in Fig. 4, which was obtained with the mixed sample of several phosphate ions. E in Fig. 4 shows the result of pyrophosphate ion.

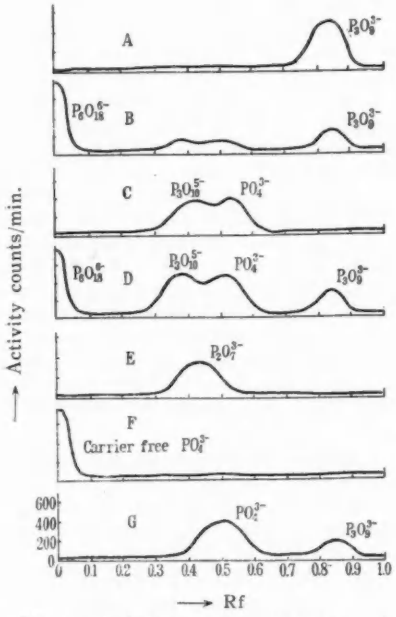


Fig. 4. Radioactive chromatogrames for several phosphates at 1-pyridine-1-water.
A. trimetaphosphate
B. hexametaphosphate C. triphosphate
D. trimeta-, ortho-, tri- and hexametaphosphate E. Pyrophosphate
F. "carrier free" orthophosphate
G. orthophosphate labelled with 'carrier free' orthophosphate.

Especially interesting cases are shown in F, G in Fig. 4. In the case of F, "carrier-free" orthophosphate was developed. The peak can be seen only at the position of its origin. In the case of G the figure was obtained with the orthophosphate ion labelled with the "carrier-free" phosphate ion just mentioned, and showed two peaks. The same result was also obtained when the trimetaphosphate was used as carrier. Judging from the results of A, B and D, the right-side peak must be due to trimetaphosphate ions and the left-side peak is large enough to be considered due to the main component; i.e. the orthophosphate ions. The peak of trimetaphosphate ion must be an impurity of the "carrier-free" orthophosphoric acid which was imported from U.S.A.

Strain[8] has already made a report on a similar fact in the case of electrochromatographic separation for calcium phosphate, but he did not clearly mention what type of ions the impurity had.

Summary

1) To separate various meta-and poly-phosphate ions respectively, pyridine-water (1:1) was found to be the most desirable developing solvent. Especially, both trimeta- and hexameta-phosphate ions can be separated from the ortho-, pyro-, and tripoly-phosphate ions, but the latter were not completely separated. The authors plan to separate them after further study of solvents.

However, by using labelled radioactive substances, it may possible to detect the impurity in synthesized phosphate or the traces of other phosphates in the main component. If the radioactive dilution method should be applied, this method may be used in determining nonactive substances. No special care was necessary in this case concerning the atom-exchange of phosphorus between active phosphate ions and non-active[1].

2) As shown in Fig. 4 it may be possible to determine hydrolysis products by the present simple method.

3) There is a certain regular relationship between the ionic structures and their Rf's. That is to say, Rf's will decrease in proportion to the increase of the number of phosphorus atoms contained in each kind of ions with chain structure, while trimetaphosphate having a cyclic structure has greater Rf value than others with chain structure.

Chemical Laboratory, Faculty of Science, Hiroshima University, Hiroshima

7) M. Kobayashi and M. Shinagawa, *Kagaku no Ryoiki*, 8, No. 2, 39 (1954).

8) T.R. Sato, W.E. Kisieleski, W.P. Norris and H.H. Strain, *Anal. Chem.*, 25, 438 (1953).

Studies on Several Phosphates from the View-point of Analytical Chemistry. V. An Electro-Chromatography on Several Meta- and Poly-phosphates labelled with P^{32}

By Mutsuaki SHINAGAWA, Junichi TAKANAKA, Yoshiyuki KISO, Aiko TSUKIJI, and Yōko MATAMA

(Received November 15, 1954)

In the previous paper[1] we reported on the separation by paper chromatography of several meta- and poly-phosphates. In this paper the behaviour of several phosphate ions in electro-chromatography is discussed. The detection of the positions to which several phosphate ions migrated was carried out with active phosphates labelled with P^{32} and was found to be made possible by decolorization caused by the formation of complex metal phosphates.

Material and Apparatus

Samples used were sodium ortho-, pyro-, trimeta-, tripoly-, and hexameta-phosphate[1,2]. Almost all the separations reported here were performed on paper moistened with a single supporting electrolyte, i.e. aqueous acetic acid or ammonium acetate. Filter paper (Toyo Rosi No. 50, size 20 cm. × 20 cm.) was employed in all the experiments described herein. Aqueous solutions permeate this paper exceptionally well and hence it was found useful in the formation of chromatograms which may be developed quickly by flow of solvant.

The control of temperature of the paper during the electrical migration was not necessary because there was no remarkable change of temperature. A dry sheet of filter paper was placed on the glass sheet (the size was equal to that of the paper) and the acetic acid solution was added until an excess was present in the paper. After a few minutes, the excess electrolytic solvent was removed with a piece of blotting paper and the mixed solutions to be investigated were then added by a sharp pointed capillary to pencilled circles on the paper.

Platinum wire electrodes were placed along both ends of the paper on which a glass sheet of the same size was placed. These two glass plates were firmly pressed together with clamps. Potential (0 to 300 V.) from an electronic rectifier was applied to these electrodes.

Detection and Identification of Several Ions

a) Tracer Method. — The migration of radioactive ions in the moist paper was followed with a thin-window G. M. Counter[1]. When the separation was complete, the moist filter paper was placed in a warm (25°~30°C) well ventilated hood and dried on a table shielded from radioactive contamination by a thick nonactive paper placed on glass sheets. The filter paper was then cut along pencilled lines and it was found that the ions had migrated parallel to the lines and had been separated. The cut papers were treated by the method reported previously[1] and hence radioactive ions separated in the filter paper were detected directly with a G. M. tube and scaler. Non-radioactive ions and acidic and basic zones in the paper were detected with suitable reagents and acid-base indicators.

b) Chemical Method. — In spot tests of phosphate ions, Feigl[3], Hanes, and Isherwood[4] have already applied the formation of molybdenum blue from complex phosphomolybdate. We were able to detect phosphate ions (0.1 to 0.05 M) simply, by using Fe (III) (0.01 to 0.005 M) and $[Fe(CN)_5]$ (IV) (0.01 to 0.05 M) as reagents. Concentrations of reagents were adjusted so they could correspond with that of the samples. Sample solutions were dropped on the filter paper and dried in air. Then iron alum solution was sprayed on uniformly and again after drying in air, $[Fe(CN)_5]$ (IV) ion solution was sprayed on. Instantly the paper turned prussian blue in colour, but the parts where phosphate ions were present remained unchanged or developed somewhat different colours as compared with the colour of the

1) M. Shinagawa, T. Takanaka, Y. Kiso, A. Tsukiji and Y. Matama, This Bulletin, **28**, 565 (1955), Presented at the 7th Annual Meeting of Chem. Soc. of Japan, April 1954.

2) L.T. Jones, *Ind. Eng. Chem. Anal. Ed.*, **14**, 536 (1942).

3) F. Feigl, "Qualitative analysis by spot test" 3rd English edition, 1947, p. 251. F. Feigl, *Z. Anal. Chem.*, **61**, 454 (1922): **74**, 386 (1928).

4) C.S.I. Isherwood, *Nature*, 164, 1107 (1949).

background. If the reagent solution were sprayed in reverse, it was possible to detect and identify phosphate ions by the difference in colours of the discoloured spots and in the widths of spot-rings, as shown in Table I.

TABLE I

SPOT TEST FOR SEVERAL PHOSPHATE IONS

Phophate ion	Colour of spot	Width of ring	Identif. Lim.
PO_4^{3-}	thin violet	narrow	10 γ
$P_2O_7^{4-}$	thin violet	diffuse	
$P_3O_9^{3-}$	deep blue	diffuse	
$P_3O_{10}^{5-}$	thin violet	wide	1.3 γ
$P_6O_{18}^{6-}$	thin blue	narrow	20 γ

Identification limit of tripolyphosphate ion was the smallest among several phosphates. Identification limits shown in Table I are minimum quantities that permit the specific detection of each ion. However when the detection was not restricted to specificity, the detection limits were much smaller.

These methods for detecting phosphate ions proved satisfactory in procedure and in specific detection and were comparable to Feigl's method[4].

This method could be applied to paper chromatography and electro-chromatography.

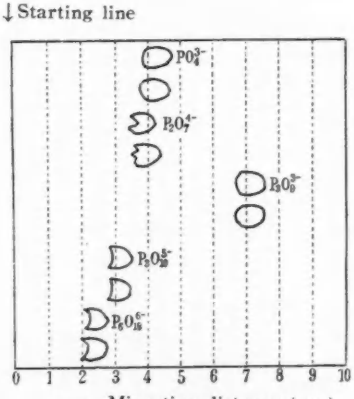


Fig. 1. Electro-chromatograms of several phosphate ions. Potential, 300 volts per 20 cm.; migration time, 2 hours; electrolyte, 0.1 mol. ammonium acetate.

Result

Fig. 1 was obtained by the detection method reported previously[3].

The vertical axis indicates the counting rate per minute and horizontal axis the migration distances of each phosphate ion. Sample concentration was about 0.05 M; the migration time, two hours; and the electrolyte concentration, 0.1 M.

Fig. 2 shows the decolorization patterns of phosphate ions which was gotten from the method of decolorization.

Fig. 1 and Fig. 2 were obtained from same experimental results.

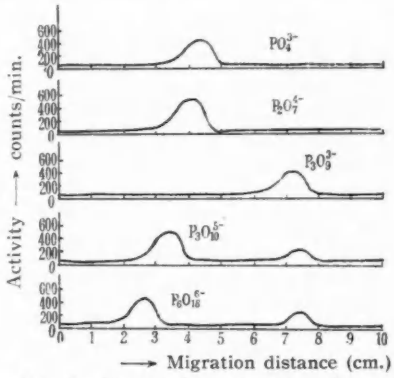


Fig. 2. Electro-chromatograms of several phosphate ions. Potential, 300 volts per 20 cm.; migration time, 2 hours; electrolyte, 0.1 mol. ammonium acetate.

Summary

1) Several phosphate ions can be separated by the present electro-chromatographic method. This method of separation is a vast improvement over the paper chromatography.

2) The smaller the number of phosphorus atoms contained in a phosphate ion, the greater the migration rate of ion in the case of chain ionic structure. Trimetaphosphate ion which has ring ionic structure showed the greatest migration rate among all of them.

3) The test by means of prussian blue was more distinct in electro-chromatography than in paper chromatography.

Chemical Laboratory, Faculty of Science, Hiroshima University, Hiroshima

The Effect of Pressure on the Semi-conductivity of Isoviolanthrone

By Hiroo INOKUCHI

(Received April 18, 1955)

On the semiconductive properties of violanthrene and related polycyclic aromatic compounds reports have been presented in the previous papers[1,2]. Since the preparations of single crystals of those compounds are very difficult and the specimens are obtained in powdered form, the measurements of electrical resistivity were usually made under compressed states. In such a condition, the apparent resistivity is likely to depend strikingly upon the compressive pressure. The relation between resistivity and pressure up to 300 kg./cm² has been reported in a preceding paper[3]. The results showed that resistivity decreases remarkably with increasing pressure up to 80 kg./cm²; however, thereafter it becomes approximately constant. A similar result was also reported by D. D. Eley et al.[4] For this and other reasons, we have assumed that the observed resistivity is an intrinsic one, excluding the contact resistance between the crystalline particles, when measurement was made beyond 80 kg./cm².

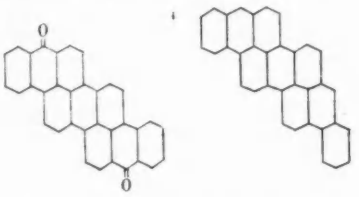
There is an interesting point concerning the pressure effect on the conductivity of organic semi-conductors. Polycyclic aromatic compounds are made of a typical molecular lattice, wherein the intermolecular force is none other than van der Waals type and not so great as compared with that in ionic or valence bond crystals. From the measurements of the heat of sublimation, the intermolecular force is found to depend on the molecular weight and 30.2 kcal./mol. for perylene and 52.3 kcal./mol. for violanthrene[5]. The compressibility is not known; however, it is presumably rather high*.

Therefore, it could be presumed that when these organic semi-conductors are compressed under high pressure, the molecules would be brought nearer to each other than the equilibrium positions and this is accompanied by further overlapping of the electron clouds (diffuse π-orbitals) or every molecule; this would have an effect on the semi-conductivity.

In this paper the effect of hydrostatic pressure up to 8,000 kg./cm² is presented.

Experimental Procedures

Among the condensed polycyclic aromatic compounds, violanthrene ($C_{34}H_{18}$) and isoviolanthrone ($C_{34}H_{16}O_2$) were selected for measurements (Fig. 1). These samples were purified as already described[3], and made into a rod, 2 mm. diameter and 6 mm. height, under ca. 300 kg./cm² pressure. This rod was supported by copper wire in a silicon oil as is shown in Fig. 2. In order to prevent silicon oil from flowing out from a gap between piston and cylinder, this contact was made carefully air-tight. Subsequently, this rod



isoviolanthrone violanthrene

Fig. 1. Isoviolanthrone and violanthrene.

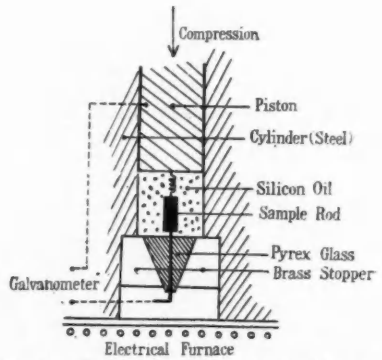


Fig. 2. A diagram of compression apparatus.

1) H. Akamatu, *Kagaku* (Iwanami), 282 (1954).
2) H. Inokuchi, This Bulletin, **24**, 222 (1951); **25**, 29 (1952); **27**, 22 (1954).
3) H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950).
4) D.D. Eley et al., *Trans. Farad. Soc.*, **49**, 79 (1953).
* The compressibility of benzene (solid) and naphthalene is $20\sim30\times10^{-6}$ (range 100 kg./cm²~1,000 kg./cm² compression)[7,8], then the volume change is 2% of its initial value under 1,000 kg./cm².
5) H. Inokuchi, S. Shiba, T. Handa and H. Akamatu, This Bulletin, **25**, 299 (1952).
6) H. Akamatu and K. Nagamatsu, *J. Colloid Sci.*, **2**, 593 (1947).
7) T.W. Richards et al., *J. Am. Chem. Soc.*, **43**, 1538 (1921).
8) H. Essex, *Z. anorg. Chem.*, **88**, 200 (1914).

was compressed by hydrostatic power with hydraulic press.

Since the compressed specimen has pretty good conductivity, the conductivity measurement was made directly without using D.C. amplifier. To know the temperature dependency of conductivity, samples were heated by electrical furnace from a room temperature up to 130°C as shown in Fig. 2.

Results and Discussion

The electrical resistivity of these organic semi-conductors decreased with compression above 300 kg./cm². The resistivity of isoviolanthrone was lowered to one five-hundredth of its value at an ordinary compression (under 80 kg./cm²~300 kg./cm² pressure). This relation is shown in Fig. 3. This decrease of resistance is of the same order as in the case of phosphorus[9] or selenium[10], that is, the decrease of resistivity of the former being to 1/1000 of its initial value with 20,000 kg./cm² compression, and that of the latter being to 1/50~1/200 under 3,000 kg./cm².

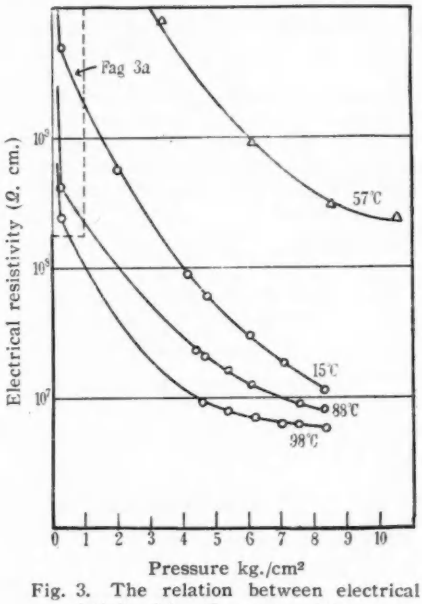


Fig. 3. The relation between electrical resistivity (ρ) and pressure (p).
△ Violanthrene
○ Isoviolanthrone

As shown in Fig. 3a, the resistivity-pressure relation curve seems reasonably to divide into two parts. The former one (I) has a deep descent between the pressure range of 0 to 80~100 kg./cm² and the latter part (II) has a mild descent above the pressure of 80~100 kg./cm². The kink point of this curve is coincident with one in which electrical resistivity is constant against pressure approximately[3]. Then it seems to be possible to suppose that the curve (I) is due to the plastic deformation of a specimen with the increasing pressure and latter part (II) is an elastic deformation of the compound.

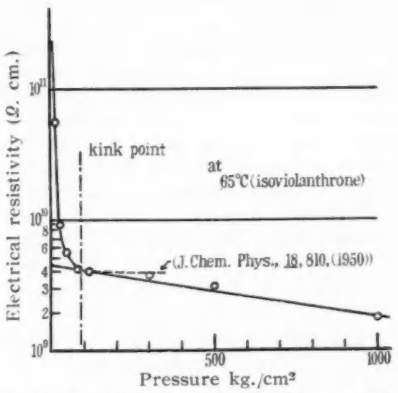


Fig. 3a. The ρ-p curve between the pressure range of 0 to 1,000 kg./cm².

Therefore, for the reason mentioned above, it seems that the intrinsic value of electrical resistivity of this group is obtained by the extrapolation of the curve (II) at the section of the axis of pressure 0 kg./cm². This value is coincident approximately with the observed one of electrical resistivity under 80 kg./cm² ~300 kg./cm² compression, and these results are consistent with the previous reports[3].

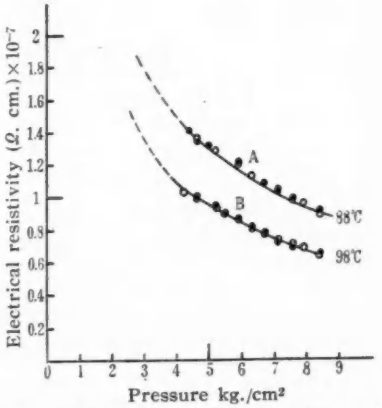


Fig. 4. The reversible curve of ρ-p relation of isoviolanthrone.
○ increasing pressure
● decreasing pressure

9) P.W. Bridgman, *Proc. Nat. Acad. Sci.*, **21**, 109 (1935).
10) F. Montén, Diss., Upsala (1909).

The change of resistivity was quite reversible to the pressure. Fig. 4 shows this relation between the electrical resistivity and the pressure from 3,000 kg./cm² to 8,000 kg./cm². From this relation, I think also that the observed decrease of electrical resistivity is an intrinsic one due to the elastic deformation of crystals, but not due to the change of crystal packing nor to any other plastic deformation.

The temperature dependency of the electrical resistivity (ρ) of these specimens has the semi-conductive character, that is,

$$\rho = \rho_0 \exp(\Delta\epsilon/2kT) \qquad (1)$$

where k is the Boltzmann's constant, T is the absolute temperature and $\Delta\epsilon$ is the activation energy. $\Delta\epsilon$, corresponds to the energy gap between the occupied level and the empty level, decreased too with increasing pressure, but as shown in Table I the change was rather small.

TABLE I
THE VALUE OF ρ_{15}° AND $\Delta\epsilon$ OF ISOVIOLANTHRONE WITH A COMPRESSION

Compression kg./cm²	ρ_{15}° Ω. cm.	$\Delta\epsilon$ kcal./mol.	$\Delta\epsilon$ e.V.
3×10^2	5×10^9	17.3	0.75
4.2×10^3	8.4×10^7	17.0	0.74
6.3×10^3	2.6×10^7	15.9	0.69
8.4×10^3	1.2×10^7	15.0	0.68

From the above results, the author inclines to assume that the increment in electrical conductivity with high pressure is contributed by electron clouds overlappings between molecules in the molecular lattice.

If the elastic constants of these organic crystals are known, and if these compounds are more compressed, we may have very interesting results.

Summary

The electrical resistivity of isoviolanthrone ($C_{34}H_{16}O_2$) and violanthrene ($C_{34}H_{18}$) decreased with compression. The resistivity of isoviolanthrone was lowered to 1/500 of its value (5×10^9 Ω.cm.) at an ordinary pressure, that is, 8.4×10^7 Ω.cm. at 4.2×10^3 kg./cm² and 1.2×10^7 Ω.cm. at 8.4×10^3 kg./cm² at 15°C. Further it is possible to suppose that the observed decrement of electrical resistivity is an intrinsic one, due to elastic deformation of crystals.

The author desires to express his hearty thanks to Prof. H. Akamatu for his kind direction of this study. The cost of this research has been defrayed from the Grant in Aid for Fundamental Scientific Research from the Ministry of Education, to which the author's thanks are also due.

Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo

Absorption Spectra of Co(III) Complexes. I. Curve Analyses of the First and Second Absorption Bands[1]

By Yoichi SHIMURA and Ryutaro TSUCHIDA

(Received April 25, 1955)

Introduction

There have been offered two experimental equations of some applicability for the broad absorption band such as the first or second absorption band[2] of metallic complexes. The one is the equation of Kuhn and Braun[3], and the other, Lowry and Hudson's[4]:

Kuhn and Braun's equation

$$\varepsilon = \varepsilon_{max} \exp\left(-\left[\frac{\nu_{max}-\nu}{\theta}\right]^2\right), \qquad (1)$$

Lowry and Hudson's equation

$$\varepsilon = \varepsilon_{max} \exp\left(-\left[\frac{\nu_{max}}{\nu}\cdot\frac{\nu_{max}-\nu}{\theta}\right]^2\right), \qquad (2)$$

1) Presented at the Symposium on Co-ordination Compounds, Tokyo, November 14, 1954.

2) For general discussion of the first and second bands of co-ordination compound the reader is requested to refer to the following literature. a) R. Tsuchida, This Bulletin, **13**, 388, 436 (1938). b) R. Tsuchida, "The Colours and Structures of Metallic Compounds", (in Japanese), Osaka, 1944. c) Y. Inamura and Y. Kondo, *J. Chem. Soc. Japan*, **72**, 843 (1951).

3) W. Kuhn and E. Braun, *Z. phys. Chem.*, **B 8**, 281 (1930).

4) T.M. Lowry and H. Hudson, *Phil. Trans.*, **A 232** 117 (1933).

where ε and ε_{max} are the formal extinction coefficients at frequencies ν and ν_{max}, ν_{max} being the frequency of maximum absorption. The value of θ is determined by the relation

$$\theta = \frac{l}{2\sqrt{\ln 2}} = \frac{l}{1.665}, \quad (3)$$

where l is the half-value width of the band, i.e., the difference between the two frequencies, ν_k and ν_l, where the formal extinction coefficients are equal to the half of ε_{max}:

$$l = \nu_l - \nu_k \quad (\nu_l > \nu_k). \quad (4)$$

The equation (1) is based upon the assumption of a symmetrical distribution in frequencies, while the equation (2) postulates a symmetrical distribution in wave-lengths.

Kuroya[5] and Shimura[6] employed the equation of Kuhn and Braun in the analyses of the spectra of Co(III) nitro- or isothiocyanato-complexes, and the Lowry and Hudson's equation was used by Mead[7] and Mathieu[8] in studying Cr(III) and Co(III) complexes. All these authors, however, adopted the equations with some modifications of the values of θ's in order to get agreement with experimental curves.

As will be seen in this paper, in fact, the first and second bands of the Co(III) complex compounds are not symmetrical either on the scale of frequency or of wave-length. An unsymmetrical equation of absorption band had been offered by Bielecki and Henri[9], but this was not superior to the equation (1) or (2). In this report, a new unsymmetrical equation has been developed and the general applicability has been substantiated by the analyses of absorption curves of the typical Co(III) complexes.

Experimental

The visible and ultraviolet absorption spectra of about fifteen typical Co(III) complexes were measured in aqueous solutions. The numerical data for the first and second bands of the complexes are collected in Table I, and typical absorption curves are shown in Figs. 1-4. The

TABLE I

ABSORPTION DATA OF THE FIRST AND SECOND BANDS OF Co(III) COMPLEXES

Type	Complex Salt	First Band				Second Band				$\Delta(\nu_{max})$	$\Delta(\log\varepsilon_{max})$
		ν_{max} (10^{13}/sec.)	$\log\varepsilon_{max}$	l (10^{12}/sec.)	δ (10^{13}/sec.)	ν_{max} (10^{13}/sec.)	$\log\varepsilon_{max}$	l (10^{13}/sec.)	δ (10^{12}/sec.)	(10^{13}/sec.)	
6N	$[Co(NH_3)_6](ClO_4)_3$	62.9	1.68	10.3	0.45	88.3	1.60	12.5	0.35	25.4	−0.08
	$[Co\ en_3](ClO_4)_3$	63.9	1.94	10.4	0.55	88.4	1.90	12.0	0.4	24.5	−0.04
	trans-$[Co\ en_2(NH_3)_2](ClO_4)_3 \cdot H_2O$	64.2	1.77	10.8	0.8	89.2	1.73	12.3	0.55	25.0	−0.04
	cis-$[Co\ en_2(NH_3)_2](ClO_4)_3 \cdot H_2O$	64.4	1.79	10.7	0.65	89.4	1.74	12.6	0.5	25.0	−0.05
5N1O	$[Co\ en_2\ glycine'](ClO_4)_2$	61.3	2.00	11.2	0.7	86.4	2.04	12.5	0.3	25.1	+0.04
	$[Co\ en_2\ leucine'](ClO_4)_2$	61.5	2.02	11.3	0.65	86.1	2.06	12.4	0.5	24.6	+0.04
4N2O	$[Co(NH_3)_4\ ox]ClO_4 \cdot H_2O$	58.7	1.91	10.4	0.5	84.0	2.11	12.3	0.35	25.3	+0.20
	$[Co\ en_2\ ox]Cl \cdot 3H_2O$	60.1	2.05	10.1	0.45	84.3	2.16	12.7	0.45	24.2	+0.11
	$[Co(NH_3)_4CO_3]ClO_4$	57.4	2.01	9.8	0.35	82.6	2.02	—*	—*	25.2	+0.01
	$[Co\ en_2\ CO_3]ClO_4$	58.4	2.13	9.4	0.3	83.0	2.09	13.3	0.0	24.6	−0.04
3N3O	α-$[Co\ glycine'_3]$**	—	—	—	—	80.4	2.16	12.1	0.35	—	—
	β-$[Co\ glycine'_3]$***	57.7	2.20	9.1	0.55	80.2	2.14	12.7	0.6	22.5	−0.06
2N4O	$[Co\ ox_2(NH_3)_2]NH_4 \cdot H_2O$	54.0	2.04	9.6	0.6	78.2	2.30	11.4	0.3	24.2	+0.26
	[Co edta] $Na \cdot 4H_2O$****	55.9	2.51	10.4	0.2	78.1	2.36	10.6	0.5	22.2	−0.15
1N5O	No example.										
6O	$[Co\ ox_3]K_3 \cdot 3H_2O$	49.7	2.17	8.0	0.35	70.9	2.30	10.8	0.65	21.2	+0.18
	$[Co(O_5Mo_6O_{18}H_6)](NH_4)_3 \cdot 7H_2O$	49.2	1.29	9.0	0.3	72.8	1.30	12.3	0.2	23.6	+0.01
	Mean.....			10.0	0.5			12.2	0.4		

* Omitted because of uncertainty. For the details, see the next paper of this series.
** The first absorption of this complex is split into two bands. The details will be reported separately.
*** Measured in 60% perchloric acid.
**** edta represents a ethylenediaminetetraacetate ion (quadrivalent).

5) H. Kuroya, *J. Inst. Polytech., Osaka City Univ.* **C 1**, No. 1, 29 (1950).
6) Y. Shimura, *J. Am. Chem. Soc.*, **73**, 5079 (1951).
7) A. Mead, *Trans. Farad. Soc.*, **30**, 1052 (1934).
8) J.-P. Mathieu, *Bull. soc. chim.*, [5] **3**, 463 (1936).
9) J. Bielecki and V. Henri, *Phys. Z.*, **14**, 516 (1913).

experimental details will appear in the next paper of this series.

In Fig. 5, the spectrum of [Co en_2 Cl_2] Cl is given. This was determined in methyl alcoholic solution with concentration of 3.3×10^{-3} F. A Beckman DU spectrophotometer was used.

Inclination of Absorption Band

Lowry and Hudson[4] previously stated that absorption spectra of most organic compounds are not symmetrical but steeper on the side of longer wave-lengths. As will be seen in Figs. 1-5, this is also true of the first and second bands of Co(III) complexes.

In order to obtain precise information about the unsymmetrical nature of these absorption bands, a new parameter, δ, was introduced (see, Fig. 1):

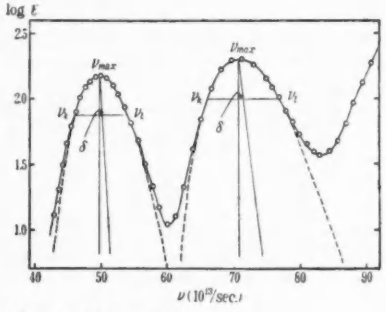


Fig. 1. $[Co\ ox_3]^{3-}$:
-o-o-o-, experimental curve;
-----, first and second bands calculated by the new equation.

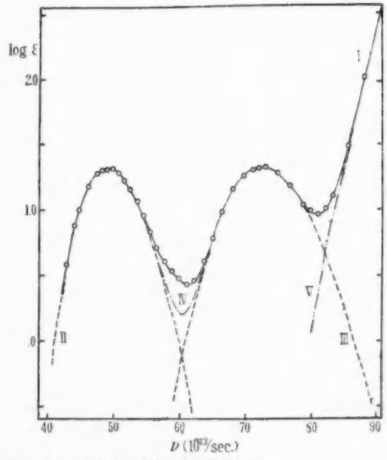


Fig. 2. $[Co(O_2Mo_6O_{19}H_6)]^{3-}$:
I, experimental curve; II, calculated first band; III, calculated second band; IV, II+III; V, I−III.

$$\delta=\frac{\nu_k+\nu_l}{2}-\nu_{max.} \qquad (5)$$

This is a measure of the inclination of the absorption band. The values of the parameters determined are given in Table I. The following conclusions were drawn from these data: (a) the values of the inclination parameters vary from 0.0 to $+0.8(\times10^{13}$/sec.). Thus the first or second bands of these complexes are almost always steeper on the side of longer wave-lengths. (b) Among the values of δ's no apparent regularities were recognized. (c) In summary, these bands are not symmetrical either on the scale of frequency or wave-length.

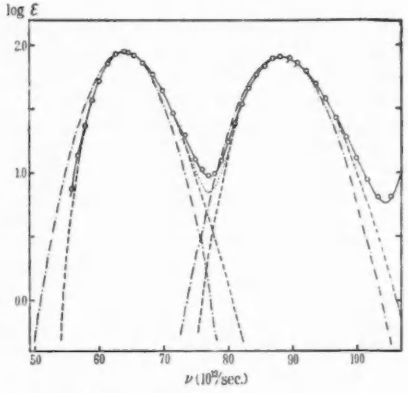


Fig. 3. $[Co\ en_3]^{3+}$:
-o-o-o-, experimental curve;
-----, calculated by the new equation;
————, calculated by Kuhn and Braun's equation.

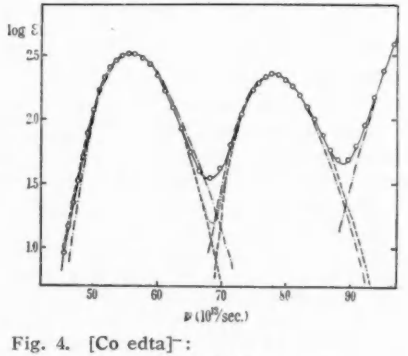


Fig. 4. $[Co\ edta]^{-}$:
-o-o-o-, experimental curve;
-----, calculated by the new equation;
————, calculated by Lowry and Hudson's equation.

Experimental Equation

To fit the unsymmetrical absorption bands, a new absorption equation (6) was developed:

$$\varepsilon=\varepsilon_{max}\exp\left(-\left[\frac{\theta-\sqrt{\theta^2-2\delta'(\nu_{max}-\nu)}}{\delta'}\right]^2\right) \quad (6)$$

where

$$\delta'=2\times0.434\times\frac{\delta}{0.3} \quad (7)$$

As in equation (1) and (2), θ is defined by the relation (3).

The principal feature of the new equation is that it is a modification of Kuhn and Braun's equation by the addition of a correction term, which contains the inclination parameter δ. Thus the equation (6) becomes

$$\nu=\nu_{max}\pm\theta'\sqrt{\log\varepsilon_{max}-\log\varepsilon}+\frac{\delta}{0.3}(\log\varepsilon_{max}-\log\varepsilon), \quad (8)^*$$

where $\theta'=\dfrac{\theta}{\sqrt{0.434}}$. If the third term is neglected, the equation (8) is reduced to the equation (1). The expression (8) has practical conveniences because it is applicable to either symmetrical or unsymmetrical bands ($\delta=0$ for symmetrical and $\delta\neq0$ for unsymmetrical).

The curve of equation (8) passes the three points (ν_{max}, ε_{max}), (ν_k, $\frac{1}{2}\varepsilon_{max}$) and ($\nu_l$, $\frac{1}{2}\varepsilon_{max}$), and adequately represents the essential characteristics of the experimental curve. Both the calculated and experimental curves for some of the Co(III) complexes are shown in Figs. 1–4. The agreement is now so close as to approach the limits of experimental error throughout the first and the second bands except where there is serious overlapping of the two bands. The values calculated by the equations (1) or (2) are also plotted for comparison (Figs. 3 and 4). From these figures, it is clear that the new equation shows a closer resemblance to the observed curves than the equation (1) or (2), especially on the side of shorter wavelengths.

The new equations are also applied successfully to the analyses of the specific absorption bands, for example, the isothiocyanato specific bands of Co(III) complexes, which will be the subject of a later paper of this series.

It should be added that integration of the equation (6) gives for the total intensity F of a broad absorption band:

$$F=\int\varepsilon d\nu=\int\varepsilon_{max}\exp\left(-\left[\frac{\theta-\sqrt{\theta^2-2\delta'(\nu_{max}-\nu)}}{\delta'}\right]^2\right)d\nu$$

$$=\varepsilon_{max}\theta\int_{-\infty}^{\infty}e^{-t^2}dt=\varepsilon_{max}\cdot\theta\cdot\sqrt{\pi}=1.06\,\varepsilon_{max}\cdot l \quad (9)$$

This formula is useful for determining experimentally the oscillator strengths of broad absorption bands.

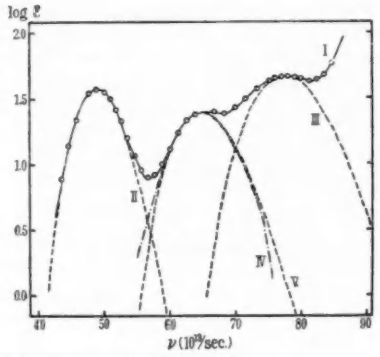


Fig. 5. *trans*-[Co en$_2$Cl$_2$]$^+$:
I, experimental curve; II, calculated first component of first bands; III, calculated second band; IV, I−(II+III); V, calculated second component of first bands.

Application to the spectra of trans-[Co en$_2$ Cl$_2$]$^+$

Recently[10,11] it was confirmed that the first absorption of *trans*-[Co en$_2$ Cl$_2$]$^+$ was spilit into two peaks, overlapping the second component on the second absorption band. The analyses of these bands using equation (8) are shown in Fig. 5. As with the first peak of the first bands, the curve II was calculated by the use of the parameters determined experimentally. For the second band, by using the mean values of the half-value widths and inclination parameters for the second bands ($l=12.2$, $\delta=0.4\times10^{13}$/sec., as listed in Table I), curve III has resulted. After subtracting curves II and III from the experimental curve I, a peak appeared at 64.9 ($\times10^{13}$/sec.) with intensity of $\log\varepsilon=1.41$. The resultant band IV was exactly reproduced by the curve V, which was calculated using the values, $l=10.5$ and $\delta=0.45$. The parameters of these bands are given in Table II.

* $\varepsilon>\varepsilon_{max}e^{-(\theta/\delta')^2}$, for $\nu<\nu_0$ if $\delta>0$ and for $\nu>\nu_0$ if $\delta<0$.

10) M. Linhard and M. Weigel, *Z. anorg. allg. Chem.*, **271**, 101 (1952).

11) S. Yamada, A. Nakahara, Y. Shimura and R. Tsuchida, This Bulletin, **28**, 222 (1955).

TABLE II
FIRST AND SECOND BANDS OF *trans*-[Co en$_2$ Cl$_2$]$^+$

Band	ν_{max} (10^{13}/sec.)	log ε_{max}	l (10^{13}/sec.)	δ (10^{13}/sec.)
First Bands				
First component	48.8	1.58	7.8	0.3
Second component	64.9	1.41	10.5	0.45
Second Band	77.5	1.68	(12.2)	(0.4)

Relation between the First and the Second Bands

i) Frequency of Maximum Absorption.—Some close relationships have been recognized between the first and the second bands of metallic complexes[12]. As regards the Co(III) complexes, Kuroya[5] and Sone[12] derived each an experimental formula for the positions of the first and the second bands:

Kuroya's formula $\nu_2=\nu_1+25.0$ (10)

Sone's formula $\nu_2=1.189\,\nu_1+13.31$, (11)

where ν_1 and ν_2 are the frequencies in 10^{13}/sec. of absorption maxima of the first and the second bands.

In Fig. 6, both the formulae are plotted

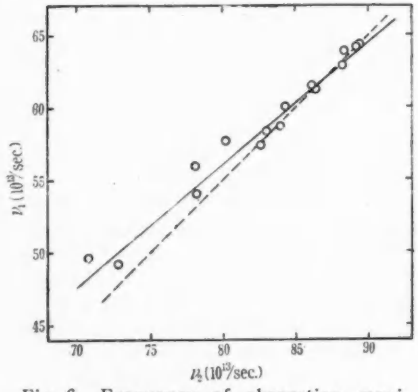


Fig. 6. Frequency of absorption maximum of the first band vs. that of the second band:
○ , experimental data;
-----, plot of Kuroya's formula;
———, plot of Sone's formula.

with the new data listed in Table I. It is seen that Sone's formula shows excellent agreement with the experimental data. From the values of $\Delta(\nu_{max})$ listed in Table I, which is the frequency difference between the maxima of the second and the first bands, it is also shown that Kuroya's formula is useful for the complexes of hexammine-, pentammine- and tetrammine-types. But the values of $\Delta(\nu_{max})$ for complexes of triammine-, diammine- and hexacido-types deviate considerably from 25.0. Such a condition is also clearly observed in Fig. 7, on the left

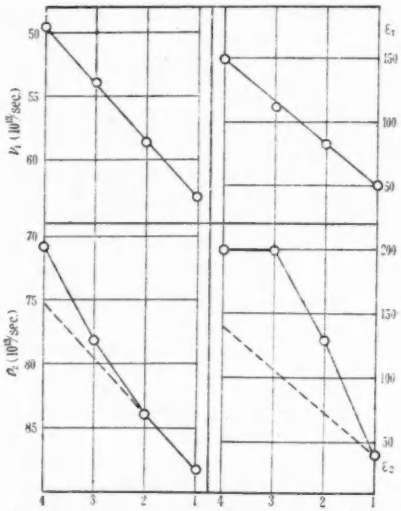


Fig. 7. Frequency positions and formal extinction coefficients of the ammine-oxalato Co(III) complexes:
1, $[Co(NH_3)_6]^{3+}$;
2, $[Co(NH_3)_4\ ox]^+$;
3, $[Co(NH_3)_2ox_2]^-$;
4, $[Co\ ox_3]^{3-}$.

part of which are plotted the frequency values for the first and second bands of Co(III) complexes belonging to an ammine-oxalato series. From the diagrams it has been confirmed that the successive substitutions of ammonia molecules by oxalate ions cause the shifts in the first absorption bands which are directly proportional to the degree of the substitution. On the other hand, the shifts in the second bands are not proportional to the degree of substitution; the greater shifts were observed for the second bands as compared with the first bands.

It is interesting to note that a similar relation exists among the absorption intensities of these complexes (See right part of Fig. 7). In view of these relations it should be suggested that the first and the second bands arise from some what different origins.

ii) Intensity.—Many previous authors recognized that the intensities of the first and the second bands are nearly of the same order. This is also supported by the values of $\Delta(\log \varepsilon_{max})$ listed in Table I ($\Delta(\log \varepsilon_{max})$ denotes the difference between log ε_{max}'s of

12) K. Sone, *J. Chem. Soc. Japan*, **71**, 270, 316 (1950).

the second and the first bands. It should be added, however, that all oxalato-complexes studied are stronger in the second bands than in the first bands.

iii) Half-value Width. — The half-value widths of the first bands are always smaller than those of the second bands (see Table I).

iv) Inclination Parameter.—The inclination parameters of the first bands are almost always greater than those of the second bands (see Table I).

Summary

The measurements of the visible and ultraviolet absorption spectra of about fifteen Co(III) complex compounds have revealed that the first and second bands of these complexes are not symmetrical either on the scale of frequency or wave-length, and that these bands cannot be represented by the equation of Kuhn and Braun, nor of Lowry and Hudson.

To fit the unsymmetrical absorption bands, a new experimental absorption equation has been developed and its adequacy substantiated.

Some relationships between the first and the second bands of Co(III) complexes are also investigated.

Department of Chemistry, Faculty of Science, Osaka University, Osaka

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Intermolecular Charge-Transfer Spectra. IV. Electronic Structure of Molecular Complexes

By Hideo MURAKAMI

(Received March 30, 1955)

As was mentioned in the previous paper[1], the observed molar extinction coefficient ϵ_c of intermolecular charge-transfer spectra decreases by a considerable amount with the increase of donor character of B-component (or that of acceptor character of A-component) in spite of the appreciable decrease of the factor $(W_1 - W_0)$. In order to solve this apparent contradiction and caculate the absorption intensity f_{EN} or ϵ_c, it was pointed out that one should take the following factors into account:

1) Electron density distribution in the molecular orbitals which are essential to the intermolecular charge-transfer spectra.

2) The degree of extension of each atomic orbital.

For example, as was stated in the previous paper, it is easy to show that these two factors make the value of resonance integral $|H_{01}|$ and consequently that of ϵ_c smaller for the substituted benzene complex than that for benzene complex. Somewhat later, Kuboyama and Nagakura also suggested the smaller value of resonance integral for naphthalene complex than for benzene complex in order to explain their own experimental results concerning heat of formation[2]. It is obvious that this suggestion can be included in the afore-mentioned statement 1) as special case.

In the present paper, the previous idea will be shown in the more concrete and quantitative form. Moreover, the predicted relative value of ϵ_c will be compared with some of the experimental results.

General Theory

In the third paper of this series[1], the simple relation between resonance energy and absorption intensity is given as follows:

$$H_{01}^2/(W_1 - W_0) \simeq (3h^2/8\pi^2 m) f_{EN}/(r_B - r_A)^2 \quad (1)$$

where f_{EN} is the oscillator strength of intermolecular charge-transfer spectra and $(r_B - r_A)$ is the distance between the respective electronic center of B- and A-component. The left hand side of the above equation represents the resonance energy between two hypothetical electronic structures $\Psi_0 = \Psi(A \cdot B)$ and $\Psi_1 = \Psi(A^- - B^+)$.

Since the resonance intergral H_{01} and the overlap integral S is given respectively by

$$H_{01} = (\Psi_0 | H | \Psi_1), \quad S = (\Psi_0 \Psi_1),$$

it is reasonable to postulate the approximate

1) H. Murakami, This Bulletin, 27, 268 (1954).

2) A. Kuboyama and S. Nagakura, *J. Chem. Soc. Japan*, 75, 1082 (1954).

proportionality between them; that is*,

$$H_{01} \simeq const.\, S \qquad (2)$$

Now it is desirable to introduce the simple molecular orbitals ϕ_A and ϕ_B which are essential to the resonance interaction or the intermolecular charge-transfer spectra. According to Mulliken[3], the charge-transfer process involves essentially the jump of one electron in a molecular orbital ϕ_B of the B-component into a previously unoccupied molecular orbital ϕ_A of the A-component, and there exists the relation

$$S \simeq 2^{1/2} S_{AB}/(1+S_{AB}^2)^{1/2} \simeq 2^{1/2} S_{AB} \qquad (3)$$

where

$$S_{AB} = (\phi_A | \phi_B).$$

In order to estimate the overlap integral S_{AB}, one should consider that the overlapping part of ϕ_A and ϕ_B in actual molecular complex is rather localized and consequently ϕ_A and ϕ_B can be devided into two parts, respectively, as follows:

$$\begin{aligned} \phi_A &= \phi_\alpha + \phi_{\alpha'} \\ \phi_B &= \phi_\beta + \phi_{\beta'} \end{aligned} \qquad (4)$$

where ϕ_α and ϕ_β is the partial molecular orbital of A- and B-component, respectively, which are overlapping with each other for a given relative configuration. Accordingly, $\phi_{\alpha'}$ and $\phi_{\beta'}$ is defined as the remaining part of them, respectively, which are not overlapping with each other. Under such a definition as above, S_{AB} is given by

$$S_{AB} = (\phi_\alpha | \phi_\beta) \qquad (5)$$

In order to develop the calculation, we introduce the following simplifing approximation:

$$\begin{aligned} \phi_\alpha &= \sum_i^l C_i^{(\alpha)} \phi_i^{(\alpha)} \simeq C_i^{(\alpha)} \sum_i^l \phi_i^{(\alpha)} \\ \phi_\beta &= \sum_j^m C_j^{(\beta)} \phi_j^{(\beta)} \simeq C_m^{(\beta)} \sum_j^m \phi_j^{(\beta)} \end{aligned} \qquad (6)$$

where $\phi_i^{(\alpha)}$ and $\phi_i^{(\beta)}$ is the constitutent atomic orbital in the partial molecular orbital ϕ_α and ϕ_β respectively. In Eq. (6), the mean effective coefficient $C_l^{(\alpha)}$ and $C_m^{(\beta)}$ is defined respectively by

$$\begin{aligned} [C_l^{(\alpha)}]^2 &= \sum_i^l [C_i^{(\alpha)}]^2 / l \\ [C_m^{(\beta)}]^2 &= \sum_j^m [C_j^{(\beta)}]^2 / m \end{aligned} \qquad (7)$$

In the present approximation, S_{AB} is given as follows,

$$S_{AE} \simeq C_l^{(\alpha)} C_m^{(\beta)} S_{\alpha\beta} \qquad (8)$$

where

$$S_{\alpha\beta} = \left(\sum_i^l \phi_i^{(\alpha)} \middle| \sum_j^m \phi_j^{(\beta)}\right).$$

The combination of Eq. (8) with Eqs. (1), (2) and (3) provides us with the formula

$$[C_l^{(\alpha)}]^2 [C_m^{(\beta)}]^2 S_{\alpha\beta}^2 / (W_1 - W_0) \simeq const.\, f_{EN}/(\gamma_B - \gamma_A)^2 \qquad (9)$$

If the rather insensitive terms $(W_1 - W_0)$ and $(\gamma_B - \gamma_A)^2$ are ignored, Eq. (9) reduces to a very simple relation

$$[C_l^{(\alpha)}]^2 [C_m^{(\beta)}]^2 S_{\alpha\beta}^2 \simeq const.\, f_{EN}. \qquad (9a)$$

Remembering the well known formula

$$f_{EN} \simeq 4.32 \times 10^{-9} \epsilon_c \Delta\nu$$

and assuming the approximate constancy of the half width $\Delta\nu$ of the absorption band, Eq. (9a) is rewritten in the form

$$[C_l^{(\alpha)}]^2 [C_m^{(\beta)}]^2 S_{\alpha\beta}^2 \simeq const.\, \epsilon_c \qquad (9b)$$

where ϵ_c is the molar extinction coefficient of the intermolecular charge-transfer spectra. Thus, the evaluation of the relative value of ϵ_c is reduced to the electron density calculation of the molecular orbitals which are essential to the intermolecular charge-transfer spectra.

Application to Some Examples

In Eq. (9b), the numerical values of $S_{\alpha\beta}^2$ and *const.* are not known. Consequently, the theoretical prediction is limited in the relative value of ϵ_c for various complexes in which A- or B-component is the same. In the present paper, we consider the former case and define the relative value k of ϵ_c as follows:

$$k = \frac{\epsilon_c \text{ of } (A \cdot Ar)}{\epsilon_c \text{ of } (A \cdot Bz)}$$

where A represents the common A-component, and Ar, Bz respectively represents any aromatic molecule and benzene as B-component.

In case of quinhydrone-type molecular complexes, it is reasonable to assume the most compact relative configuration between two components in which the ring portion of each component is facing and contacting with the other and the substituted groups in both components are also facing with each other so long as such a configuration is allowed (see the discussion in the preceding paper[1]). Since the spatial extension of $2p$-atomic orbital of oxygen or nitrogen is considerably smaller than that of carbon, we can expect very small overlap integrals between substituted groups even in the above-described

* In the following, the numerical value and the physical dimension of *const.* should be considered for the respective case and it is not necessary to be equal throughout the every cases.

3) R.S. Mulliken, *J. Am. Chem. Soc.*, 74, 811 (1952).

configuration and can neglect them. Consequently, ϕ_B corresponds to the appropriate linear combination of $2p\pi$-atomic orbitals of ring carbon and does not contain the atomic orbitals in the substituted groups. When B-component is benzene, there exists the relation

$$\phi_B=\phi_\beta, \quad \sum_j^n[C_j^{(\beta)}]^2=1$$

as special case.

Moreover, it is reasonable to assume that $S_{\alpha\beta}$ is approximately the same regardless of the molecular size of B-component since the electronically interacting area is the same throughout the molecular complexes considered so long as the A-component is common. which is essential to the intermolecular charge-transfer process is the highest occupied one. Fortunately, the electron density distribution of the highest occupied molecular orbital have been calculated by Fukui et al. for various aromatic compounds in relation to their reactivity as frontier electron theory[5]. From Eq. (10), it is easy to see that k is given by the half of the total electron density in the partial molecular orbital ϕ_β since the complete orbital ϕ_B is filled by two electrons. By using the numerical value of Fukui et al., one can easily predict the approximate value of k for various molecular complexes. Some examples are shown in Table I together with the experimental results. The agreement between

Table I

Observed and calculated values of the ratio k of molar extinction coefficient ϵ_c in various molecular complexes

A-Component	B-Component	ϵ_c	$k_{obs.}$	$k_{calc.}$	Reference
p-Quinone	Benzene	(2800)[a]	1.00	1.00	(1)
	Phenol	1200	0.43	0.66[b]	(2)
	Hydroquinone	890	0.32	0.32	(2)
Maleic anhydride	Benzene	3140	1.00	1.00	(1)
	Styrene	1940	0.62	0.50	(1)
	Dimethylaniline	1590	0.51	0.66[b]	(1)
Iodine	Benzene	16400	1.00	1.00	(3)
	Dibenzyl	11200	0.68	1.00	(3)
	Bromobenzene	10400	0.63	0.66[b]	(3)
	Styrene	7350	0.45	0.50	(3)
	Stilbene	7140	0.44	0.31	(3)
	Naphthalene	7640	0.47	0.50	(3)

a) Extrapolated value (not so exact)

b) Estimated from Fig. 5 in reference 5) assuming the equal electron density at 1- and 4-positions. (Assumed values of parameter are $a\simeq 0.6$, $b=1.0$. Of course, these values may differ more or less for the different compounds and consequently the predicted values of k may also deviate from the listed value 0.66.)

(1) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **75**, 3776 (1953).
(2) H. Tsubomura, This Bulletin, **26**, 304 (1953).
(3) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952).

These situations enable us to give a simple expression for k, that is,

$$k=\sum_j^m[C_j^{(\beta)}]^2. \qquad (10)$$

This formula is also applicable to the halogen-aromatic complexes since the dimension of the halogen molecule is almost the same as that of the benzene ring.

As was discussed by McConnell et al., there is an excellent correlation between the wavelengths of absorption maximum of intermolecular charge-transfer spectra and the estimated ionization potentials of B-components[4]. Therefore, it is almost certain that the molecular orbital in the B-component predicted and observed values are relatively good at least qualitatively. From the quantitative point of view, however, one should remember the existence of the following situations which prevent the exact comparison:

1) The simplifing assumption such as Eq. (6) is introduced.

2) The insensitive terms $1/(W_1-W_0)$ and $1/(\gamma_B-\gamma_A)^2$ are neglected although in some cases they might not be negligible.

3) In the present consideration, k is defined as the ratio of ϵ_c for convenience, sake although it should be defined as that of f_{EN} from the more exact point of view.

4) The statistical situation on the relative

4) McConnell, Ham and Platt, *J. Chem. Phys.*, **21**, 66 (1953).

5) Fukui, Yonezawa, Nagata and Shingu, *J. Chem. Phys.*, **22**, 1433 (1954).

configuration between two components is neglected.

At any rate, it is almost certain that the interesting behavior of ϵ_c among such molecular complexes as shown in Table I is explainable by the consideration of their electronic structures.

Appendix

In case of iodine-benzene complex, the observed value of oscillator strength ($f_{EN} \simeq 0.38$) is very large. Consequently, Eq. (1) seems to predict the much larger resonance energy than the observed heat of formatian ($\Delta H \simeq 1.4$ Kcal./mol.[6]). This apparent contradiction can be solved by the examination of its electronic structure.

According to Mulliken, the attractive resonance energy in halogen-benzene complex (symmetry C_{2v}) is essentially given by the electronic interaction between antibonding σ-orbital $b_2\sigma_u$ in halogen molecule and the molecular orbital which has the same symmetry b_2 in benzene[3]. Therefore, the electronic interaction between any other pair of orbitals (especially that of π-orbitals) which are occupied by electrons contribute to exchange repulsive interaction. (In the rough approximation, the contribution of excited electronic configurations can be neglected since the degree of contribution of them is expected to be small.)

Now we examinc the geometrical situation of each atomic orbital in halogen molecule. As is well known, the electron density distribution of σ-orbital is rather concentrated on the molecular axis, on the contrary, that of π-orbital is extended to the direction which is normal to the molecular axis. Taking this fact into account and assuming the most compact relative configuration, it is quite reasonably expected that the attractive resonance energy is negligibly small even at the region (distance between two components) in which the exchange repulsive energy amounts to considerable value. This situation is expressed

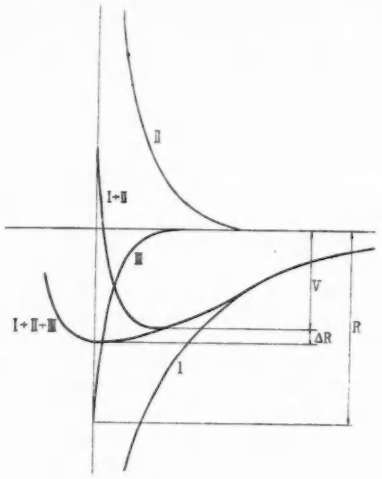

Fig. 1.

in Fig. 1 diagramatically. In this figure, the curve I, II and III represents, respectively, the ponential energy curve of van der Waals type attraction, exchange repulsion and resonance attraction. Comparing the resultant curve (I+II) and (I+II+III), it is easy to see that the contribution of resonance attraction (ΔR) to the total binding energy ($V+\Delta R$) is small enough although the absolute value of resonance energy (R) in equilibrium position is very large. This situation seems to suggest the special importance of the repulsive term in the charge-transfer type interaction.

The author wishes to express his sincere thanks to Prof. S. Akabori for his encouragement and interest in the course of this study.

Department of Chemistry, Faculty of Science, Osaka University, Osaka

6) T.M. Cromwell and R.L. Scott, *J. Am. Chem. Soc.*, 72, 3825 (1950).

Intermolecular Charge-Transfer Spectra. V. Halogen-Polymethylbenzene Complexes

By Hideo MURAKAMI

(Received March 30, 1955)

In the first paper of this series[1], we studied the spectroscopic features of halogen-aromatic complexes such as $X_2 \cdot C_6H_{(6-n)}(CH_3)_n$ in which $n=0, 1, 2$. Now we extend the previous discussions over the cases of $n=3, 4, 5, 6$ and compare the predicted value of molar extinction coefficient ϵ_c of intermolecular charge-transfer spectra with the observed results. Next, the foregoing idealized treatment will be discussed from the more general point of view in relation to the previous discussions on pressure effect[2,3] and the recent result by Ham[4].

Statistical Consideration

As can easily be seen, the electronic structure of π-electron system in methyl-benzene is practically the same as that in benzene itself. Consequently, in case of halogen-alkylbenzene complex, the observed behaviour of ϵ_c cannot be explained from the viewpoint of the electronic structure of the aromatic component. In order to solve this difficulty, we have already introduced the statistical treatment on the relative configuration between the two components[1]. That is, we considered the two relative configurations such as Model (α) and Model (β). In Model (α), the halogen molecule is resting on the benzene ring with its axis parallel to the plane of benzene and its center on the six-fold axis of benzene. In Model (β), the center of the halogen molecule is shifted towards the methyl group on account of van der Waals attraction of it (see Fig. 1 in reference 1). Since the degree of overlapping between orbital functions which are essential to charge-transfer interaction is considerably different for Models (α) and (β), it is reasonable to assume that each configuration has its own molar extinction coefficient $\epsilon_c^{(\alpha)}$ and $\epsilon_c^{(\beta)}$, respectively.

Next we postulate, as we have already done in our previous paper[1], that these two configurations (α) and (β) have almost the same stability and exist in solution with almost equal statistical weight. This assumption is reasonable so long as the contribution of the van der Waals type interaction is predominant compared with that of the charge-transfer type interaction[5]. Considering these conditions, we can give the following general formula for the observed molar extinction coefficient ϵ_c of molecular complexes as statistical mean,

$$\epsilon_c=(\epsilon_c^{(\alpha)}+n\epsilon_c^{(\beta)})/(1+n) \qquad (1)$$

where n is the number of substituted methyl groups and arbitrary integer between 0 and 6. At the present stage, the exact evaluation of $\epsilon_c^{(\beta)}$ is somewhat difficult and remains as parameter. Hence, we retain the previous relation[1]

$$\epsilon_c^{(\beta)} \simeq \epsilon_c^{(\alpha)}/2 \qquad (2)$$

as a reasonable one. The value of $\epsilon_c^{(\alpha)}$ is approximated by the observed molar extinction coefficient of halogen-benzene complex ($n=0$). Then, Eqs. (1) and (2) enable us to predict the observed molar extinction coefficient ϵ_c for any value of n. The results are shown in Table I together with the experimental results. At present, we have two sets of experimental results. The one is by Andrews and Keefer[6] and the other is by Tamres et al.[7]

As is seen in Table I, the order of magnitude of predicted values corresponds well to either of the two observations. The most essential feature of theoretical prediction is the decrease of ϵ_c with the increase of n. This interesting feature is well established in the data of Tamres et al. although it is not established in those of Andrews and Keefer. Strictly speaking, the rate of decrease of observed ϵ_c is greater than that of theoreticol prediction. If this difference is significant, it may probably be due to the contribution of the configurations in which the halogen molecule is rather resting on the

1) H. Murakami, This Bulletin, **26**, 441 (1953).
2) R.E. Gibson and H. Loeffler, *J. Am. Chem. Soc.*, **62**, 1324 (1940).
3) H. Murakami, This Bulletin, **26**, 446 (1953).
4) J. Ham, *J. Am. Chem. Soc.*, **76**, 3881 (1954).
5) H. Murakami, This Bulletin, **28**, 577 (1955).
6) L.J. Andrews and R.M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952).
7) M. Tamres, D.R. Virzi and S. Searles, *J. Am. Chem. Soc.*, **75**, 4358 (1953).

TABLE I
EXPERIMENTAL AND THEORETICAL MOLAR EXTINCTION COEFFICIENTS OF IODINE-POLYMETHYLBENZENE COMPLEXES (IN CCl_4 SOLUTION)

Aromatic Component	ϵ_c (obs.) Andrews et al.[3]	ϵ_c (calc.)	ϵ_c (obs.) Tamres et al.[7]	ϵ_c (calc.)
Benzene	16400	(16400)	14700	(14700)
Mesitylene	8850	10250	10200	9190
Durene	9000	9840	8700[a]	8820
Pentamethylbenzene	9260	9570	7770	8580
Hexamethylbenzene	8200	9370	6690	8400

a) The value for isodurene.

two adjacent methyl groups and its own molar extinction coefficient is smaller than $\epsilon_c^{(\beta)}$.

If methyl groups are replaced with ethyl groups, one can expect the larger contribution of such configurations (which have smaller ϵ_c than $\epsilon_c^{(\beta)}$). Moreover, as was pointed out by Andrews and Keefer and also by Tamres et al., the steric hindrance of ethyl groups prevent the configuration such as Model (α) (which has greater ϵ_c than $\epsilon_c^{(\beta)}$). Consequently, one can predict the smaller ϵ_c for $X_2 \cdot C_6(C_2H_5)_6$ than for $X_2 \cdot C_6(CH_3)_6$. In fact, Tamres et al. observed the much smaller ϵ_c for $X_2 \cdot C_6(C_2H_5)_6$ ($\epsilon_c \sim 4570$) than for $X_2 \cdot C_6(CH_3)_6$ ($\epsilon_c \sim 6690$). On the contrary, Andrews and Keefer observed the reverse, that is, $\epsilon_c \sim 16700$ for the former complex. Judging from the regular behaviour of the observed ϵ_c and K, the results by Tamres et al. seem to be more reliable. At any rate, further experimental study is very desirable.

Generalization and Pressure Effect

In the foregoing discussion, we considered only two configurations such as Model (α) and Model (β). This corresponds to the idealized limiting case and is not exact enough. From the more general point of view, the observed molar extinction coefficient ϵ_c is given as follows:

$$\epsilon_c = \sum_i W_i \epsilon_c^{(i)} / \sum_i W_i \qquad (3)$$

where $\epsilon_c^{(i)}$ is the molar extinction coefficient for the any configuration (i) and W_i is the statistical weight of this configuration in solution. In case of non-substituted benzene complex, the value of W_i which corresponds to such a configuration as Model (β) may be much smaller than that of Model (α). On the other hand, in case of substituted benzene complex, the former value may become comparable to the latter one. Then, if one assumes that W_i of all the configurations except those of Model (α) and Model (β) are equal to zero, Eq. (3) reduces essentially to Eq. (1)*. In practice, any of W_i may be unequal to zero although it may be small enough. Consequently, when one uses the observed ϵ_c of halogen-nonsubstituted benzene complex as the value of $\epsilon_c^{(\alpha)}$ in Eq. (1), one should always remember that such a value of $\epsilon_c^{(\alpha)}$ has already included the statistical effect more or less (the assumed value of $\epsilon_c^{(\beta)}$ should also be considered as effective value which includes statistical effect).

This situation seems to have special importance for the explanation of pressure effect. In fact, it is reasonable to consider that the high pressure favours the compact configurations and makes the values of W_i of compact configurations greater. In case of halogen-aromatic complexes, the more compact configuration may have the greater $\epsilon_c^{(i)}$. Taking these factors into account, one can predict the increase of ϵ_c with increase of pressure. These considerations correspond to the special case of pressure effect which was discussed in the second paper of this series and seems to explain the recent work by Ham in which he observed the slight increase of optical density under the high pressure for iodine-aromatic complexes in *n*-heptane solution.

According to our opinion, the above-described explanation is more correct than that of Ham which postulated the alteration of equilibrium constant K and the constancy of ϵ_c with increase of pressure. At least, we should emphasize that Ham's explanation is rather macroscopic or phenomenological and does not take the microscopic situation into account: such as relative configuration between two components which seems to be essential to the value of ϵ_c. Especially, Ham's discussion seems to be inadequate for the case of Gibson and Loeffler's experiment in

* If one takes the contribution of Model (γ) into account—see Part I of this series—the contribution of Model (α) and Model (β) should decrease by the corresponding amount.

which 50%, 50% mixture of nitrobenzene and aniline was used (without solvent). In such a condition as the above, the degree of intensification of ϵ_c may become much greater than that in Ham's experiment which was performed as dilute solution (solvent was *n*-heptane). Moreover, Gibson and Loeffler observed that the elevation of temperature at constant volume causes the same result as the high pressure at constant temperature. It is almost certain that the elevation of temperature tends to break up the molecular complex in the usual concept even at constant volume. Consequently, the concept or definition of molecular complex should be generalized as was discussed by Gibson and Loeffler from the kinetic point of view. If one admits this generalization, the previous explanation in the second Part of this series seems to be most probable.

The author wishes to express his sincere gratitude to Prof. S. Akabori for his ceaseless interest and encouragement throughout the course of this series.

Department of Chemistry, Faculty of Science, Osaka University, Osaka

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On the Molecular Rotations of Polypeptides of Alanine. II.

By Hideo MURAKAMI

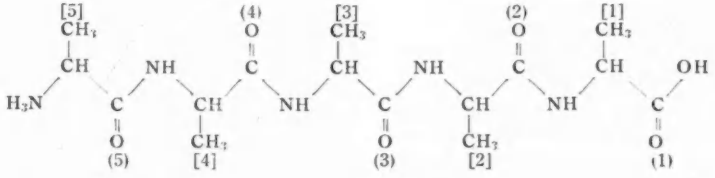
(Received April 1, 1955)

Introduction

In the previous paper, the molecular rotations $[M]_D$ of a series of polypeptides of alanine were calculated theoretically assuming the folded α-type configuration[1]. More precisely, the seven membered ring due to intramolecular hydrogen bond was assumed so as to satisfy Kauzmann and Eyring's suggestion in which the rigid ring structure of polypeptides was required[2]. The recent viewpoint, however, is that one can expect a rather rigid nature even in the extended β-type configuration[3]. Therefore, it seems to be desirable to calculate the molecular rotation for the extended configuration assuming the complete rigidity. As was already shown, the contribution of the one-electron effect is much smaller than that of the dynamical coupling effect. Consequently the calculation will concern only the latter effect.

Method of Calculation

As a molecular model, the extended β-type configuration is used. For example, the configuration of tetra-alanyl-alanine is given by the formula:



Here, one can consider two idealized models. First, the structure completely rigid from one end to the other, $\beta_{(1)}$. Second, the structure in which only the two terminal groups (COOH and $CH(CH_3)$ (NH_3)) are in the state of free rotation and the remaining part being completely rigid, $\beta_{(2)}$.

The method of calculation and the degree of approximation are the same as before* and the following pairs of interactions are taken

1) H. Murakami, This Bulletin, **27**, 246 (1954).
2) W. Kauzmann and H. Eyring, *J. Chem.Phys.*, **9**, 41 (1941).
3) M. Laskowski, Jr., and H.A. Scheraga, *J. Am. Chem. Soc.*, **76**, 6305 (1954). In this paper, the authors stated as follows: "For rotation in hydrocarbons the potential barriers are quite high compared to *RT* at room temperature. Further, since the potential curves for internal rotation in higher hydrocarbons are, in general, asymmetric and the various potential minima differ appreciably, we can assume that the majority of nonhydrogen bonded molecules are confined to the lowest minimum and that the entropy associated with the distribution among various possible minima is small." (See p. 6308).

* In order to simplify the calculation, the bond angles in the main chain are all assumed to be 120°. This is the only difference from the previous approximation.

into account.*

A: {(1)[1]} {(2)[2]} {(3)[3]} {(4)[4]} {(5)[5]}
B: {(2)[1]} {(3)[2]} {(4)[3]} {(5)[4]}
C: {(3)[1]} {(4)[2]} {(5)[3]}
D: {(1)[2]} {(2)[3]} {(3)[4]} {(4)[5]}

The molecular rotations $[M]_D$ are given for $\beta_{(1)}$ and $\beta_{(2)}$, respectively, as follows:

$\beta_{(1)}$	alanine	A
	alanyl-alanine	$2A+B+D$
	di-alanyl-alanine	$3A+2B+C+2D$
	tri-alanyl-alanine	$4A+3B+2C+3D$
	tetra-alanyl-alanine	$5A+4B+3C+4D$
$\beta_{(2)}$	alanine	0
	alanyl-alanine	B
	di-alanyl-alanine	$A+2B+C$
	tri-alanyl-alanine	$2A+3B+2C+D$
	tetra-alanyl-alanine	$3A+4B+3C+2D$

The numerical results are shown in Tables I and II together with the previous results on the α-type cofiguration and the observed results[4].

TABLE I

Polypeptides	Calculated values $[M]_D^{\alpha}$	$[M]_D^{\beta(1)}$	$[M]_D^{\beta(2)}$	Observed values $[M]_D$
alanine	0°	− 182°	0°	− 13°
alanyl-alanine	169°	− 521°	− 143°	+ 58°
di-alanyl-alanine	380°	− 823°	− 431°	+179°
tri-alanyl-alanine	609°	−1125°	− 733°	+347°
tetra-alanyl-alanine	837°	−1427°	−1035°	+494°

TABLE II

Polypeptides	Calculated values $[M]_D^{\alpha}\times 0.591$	$-([M]_D^{\beta(1)}-A)\times 0.382$	$-[M]_D^{\beta(2)}\times 0.491$	Observed values $\|[M]_D\|+13°$
alanine	0°	0°	0°	0°
alanyl-alanine	100°	129°	70°	71°
di-alanyl-alanine	225°	245°	212°	192°
tri-alanyl-alanine	360°	360°	360°	360°
tetra-alanyl-alanine	495°	476°	508°	507°

Discussion on the Results

The noticeable features of the theoretical predictions are as follows:

1) The signs of $[M]_D$ for α-and β-type configurations are reverse (see Table I).

2) Except for the sign, the qualitative tendency of the predicted $[M]_D$ agrees relatively well with the observed one for either the configurations of α and β (see Table II).

3) The absolute values of the predicted $[M]_D$ are too great for either the configurations of α and β** (see Table I).

These results may probably require the existence of equilibrium between α-and β-type configurations***. Especially, it is interesting to observe that the predicte values based on $\beta_{(2)}$ agree very well with the experimental results in its qualitative tendency (see Table II). This fact seems to suggest the rather predominant contribution of $\beta_{(2)}$-type configuration in water solution (if this situation is proved to be correct, some statements in the previous paper must be revised within the suitable range). At the present stage, however, it is difficult to give a decisive conclusion about the direction and the degree of shift of equilibrium among various rotational isomers. In order to obtain the detailed knowledge about this equilibrium, further refinement of calculation is necessary and the determination of the absolute configuration of alanine or related amino acid is very desirable. This is a task for future study.

The author wishes to express his sincere gratitude to Prof. S. Akabori for his kind guidance and encouragement throughout the course of this study.

Department of Chemistry, Faculty of Science, Osaka University, Osaka

* Pairs $E\{(4)[1]\}\{(5)[2]\}$ are neglected since these pairs correspond to too large separation in case of β-type configuration.

4) P.A. Levene and P.S. Yang, *J. Biol. Chem.*, **99**, 405 (1932). See also E. Abderhalden and W. Gohdes, *Ber.*, **64**, 2070 (1931).

** At the present stage, the values of parameters are not conclusive. Moreover, the degree of rigidity of β-type configuration is still a matter of doubt. Therefore, one should remember that the absolute value of the predicted $[M]_D^{\beta(1)}$ and $[M]_D^{\beta(2)}$ are also inconclusive.

*** Strictly speaking, the contribution of intermediate type configurations—folded and extended configurations are mixed in the one polypeptide chain—should also be considered. In the rough approximation, however, one can replace the intramolecular distribution of α- and β-type configurations by the statistically equivalent intermolecular ones.

Determination of Carbon in Organic Compounds by the Iodic Acid Decomposition Method

By Shigeru OHASHI

(Received June 21, 1955)

In the previous papers the author and his co-workers have already reported that by using a mixture of potassium iodate and strong phosphoric acid, elementary carbons[1], oxidation values of organic compounds[2], and nitrogen in organic compounds[3,4] can be simply and rapidly determined. Among these methods the determinations of carbon contents in elementary carbons, such as graphite, active carbon and so on, containing some inorganic substances, and those of oxidation values of organic compounds composed of carbon, hydrogen, and oxygen are based on the following reactions, respectively,

$$5C+4HIO_3=5CO_2+2H_2O+2I_2$$

$$5C_kH_mO_n+2(2k+m/2-n)HIO_3 = 5kCO_2+(2k+3m-n)H_2O + (2k+m/2-n)I_2.$$

Carbon contents in elementary carbons as well as oxidation values of organic compounds can be indirectly determined by titrating the liberated iodine in the above reactions.

If it is possible to estimate the liberated carbon dioxide by any suitable method in the above-mentioned reactions, it may be possible to determine directly the carbon contents in elementary carbons and in organic compounds.

The present investigation has aimed at establishing a new direct method for the determination of carbon in organic compounds by means of iodic acid decomposition followed by titrimetric estimation of the liberated carbon dioxide. The investigation on the direct determination of carbon in elementary carbons is now undertaken in this laboratory and will be reported later.

For the present study the investigation of direct semimicrodetermination of oxygen in organic substances achieved by R. D. Hinkel and R. Raymond[5] serves as a good reference. They described the fact that carbon monoxide formed in the pyrolysis of an organic compound is oxidized with iodine pentoxide, the resulting carbon dioxide is absorbed in a measured excess of 0.05 N alkali, and the excess is back-titrated with 0.025 N acid after precipitation of the carbonate formed with barium chloride.

In the present investigation, using a carbon dioxide absorber of a special type and an anhydrous sodium thiosulfate-filled iodine absorber, which were devised by Hinkel and Raymond, satisfactory results have been obtained. In this paper the recommended apparatus, reagents, and procedure for this method, the analytical results of several organic compounds, and the discussion concerning them are described.

Apparatus

The apparatus used in this study is illustrated in Fig. 1. It is mainly composed of three parts, a reaction vessel A, a carbon dioxide absorber B, and an iodine absorber K.

Into the reaction vessel A a gas-introducing tube H and a thermometer F, which is covered with a thermometer-protecting tube G, are inserted. These tubes are attached to the vessel A with rubber tubes. After passing through a concentrated solution of sodium hydroxide, a soda lime-filled tube, and concentrated sulfuric acid in turn, the air free from carbon dioxide is introduced by means of a suction pump into the vessel A through the three-way stopcock D of a water-addition funnel C, which is used to add water to the vessel A after the decomposition of a sample. The vessel A is heated at the bottom with a samll electric heater J, the temperature of which can be regulated with a transformer. The left arm of the vessel A is connected to the absorber B through the iodine absorber K filled with anhydrous sodium thiosulfate and a stopcock L.

The carbon dioxide absorber B is the same one that was used by Hinkel and Raymond. The tube B is closed at the top by means of a rubber stopper, through which the capillary tips of two burets, Q and N, containing standard solutions of hydrochloric acid and sodium hydroxide, respectively, and the tip of a reagent-addition tube R are inserted. The standard solution of sodium hydroxide is introduced from its reservoir to the buret by the compressed air. At the top of the buret N and the left side arm of the absorber B there are soda lime-filled guard tubes, P and S.

1) T. Kiba, S. Ohashi, T. Takagi, and Y. Hirose, *Japan Analyst*, 2, 446 (1953).
2) S. Ohashi, This Bulletin, 28, 171 (1955).
3) S. Ohashi, ibid., 28, 177 (1955).
4) S. Ohashi, ibid., 28, 537 (1955).
5) R.D. Hinkel and R. Raymond. *Anal. Chem.*, 25, 470 (1953).

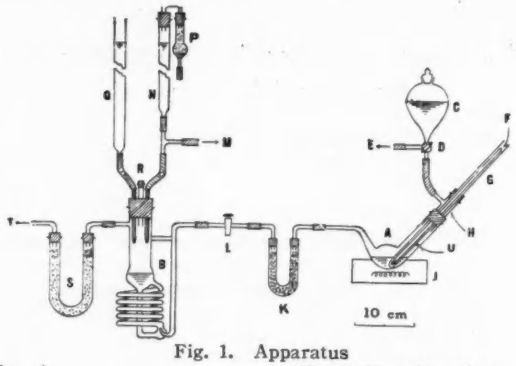


Fig. 1. Apparatus

A: Reaction Vessel
B: Carbon Dioxide Absorber
C: Water-Addition Funnel
D: Three-Way Stopcock
E: To an Apparatus Preparing the Carbon Dioxide-Free Air
F: Thermometer
G: Thermometer-Protecting Tube
H: Gas-Introducing Tube
J: Electric Heater
K: Iodine Absorber
L: Stopcock
M: To a Sodium Hydroxide Reservoir
N: Buret of Sodium Hydroxide
P: Soda Lime-Filled Guard Tube
Q: Buret of Hydrochloric Acid
R: Reagent-Addition Funnel
S: Soda Lime-Filled Guard Tube
T: To a Suction Pump
U: Small Glass Hook

Reagents

Potassium Iodate.—Extra pure grade potassium iodate was used.

Strong Phosphoric Acid.—About 400 g. of extra pure grade 89% orthophosphoric acid was dehydrated by heating until the temperature of the liquid reached 320°C. Its specific gravity was 1.96.

Anhydrous Sodium Thiosulfate.—Sodium thiosulfate having 5 mol. of water of crystallization was dehydrated in vacuo at 40°C on a water bath. The resulting white anhydrous salt was crushed and its coarse fraction was used.

Standard Solution of Hydrochloric Acid.—A 0.1 N hydrochloric acid solution standardized against pure anhydrous sodium carbonate was used.

Standard Solution of Sodium Hydroxide.—A 0.1 N sodium hydroxide solution standardized against 0.1 N hydrochloric acid described above was used. According to Hinkel and Raymond, the sodium hydroxide pellets used must contain at least 2.5% by weight of sodium carbonate. If this quantity is not present, an appropriate amount should be added to the solution. The standardization was carried out by means of the method described in the section of procedure.

Barium Chloride.—A 10% solution of extra pure grade barium chloride was used.

Thymol Blue.—A 0.1 % solution of thymol blue was used.

Procedure

Weigh accurately a 10 to 60 mg. of sample, depending upon its carbon content, into a small weighing tube; choose the sample weight so that the liberated carbon dioxide will consume about 50% of the sodium hydroxide used. Add 4 to 5 ml. of strong phosphoric acid and two or three times as much of the theoretically required amount of potassium iodate into the vessel A. Into the carbon dioxide absorber, and 3 drops of the indicator solution of thymol blue. Hang the weighing tube containing the sample on the small glass hook U of the thermometer-protecting tube G. Connect all of the apparatus and make sure that it is tight. Sending carbon dioxide-free air from E through the apparatus by a suction pump, expel all the air containing carbon dioxide, present in it. Then add 25 ml. of 0.1 N sodium hydroxide to the absorber B from the buret N.

Stop the suction, close the stopcock D, and open the stopcock L a little. Let the weighing tube containing the sample fall in the reaction medium by rotating the thermometer-protecting tube G. Then, gently heat the bottom of the vessel A with a small electric heater J. During the decomposition reaction keep the temperature of the reactants between 180° and 230°C, and regulate the stopcock L so that 2 bubbles of gas per second pass through the inlet of the absorber B. The greater part of the liberated iodine is sublimed and condensed on the inside wall of the vessel A. The small part of it is sent to the tube K and absorbed on anhydrous sodium thiosulfate. After the end of the decomposition reaction, stand the vessel A aloof from the heater until the temperature of the reaction medium falls to about 140°C. Apply gentle suction and open the stopcock D to introduce about 10 ml. of carbon dioxide-free water into the vessel A. Then heat once more the aqueous solution in the vessel A on the heater to expel the remaining carbon dioxide in the reaction medium. Then take away the heater and continue drawing air through the apparatus, at the rate of 2–3 bubbles per second for about fifteen minutes, in order to

get all the carbon dioxide into the absorber B.

From the reagent-addition tube R quickly add 10 ml. of 10% barium chloride to the absorber solution and close the top of the tube R. Then, applying rapid suction, titrate the remaining sodium hydroxide with 0.1 N hydrochloric acid until the blue color of thymol blue is changed to the light yellow one.

From the volumes of 0.1 N sodium hydroxide and 0.1 N hydrochloric acid used in the experiment the carbon content of the sample is calculated.

The standardization of 0.1 N sodium hydroxide is carried out as follows. After removing the air containing carbon dioxide from the apparatus, 25 ml. of 0.1 N sodium hydroxide, 3 drops of the indicator solution, and 10 ml. of 10% barium chloride are added to the absorber B and this solution is titrated with 0.1 N hydrochloric acid, stirring the contents of the absorber B by letting the carbon dioxide-free air flow rapidly.

Results and Discussion

At first, in order to examine the purity of the carbon dioxide-free air used in this study, after passing the air through a measured amount of 0.1 N sodium hydroxide in the absorber B for twenty to forty minutes, it was titrated with 0.1 N hydrochloric acid in the same manner as in the standardization of sodium hydroxide described above. As shown in Table I the ratios of the volumes

Table I
Examination of the Purity of the Carbon Dioxide-Free Air Used

Aeration min.	0.1 N HCl ml. / 0.1 N NaOH ml.
0	1.000
20	0.999_8
30	0.996_7
30	1.002_4
40	1.000_4

of 0.1 N sodium hydroxide and 0.1 N hydrochloric acid were almost equal to that in the case without aeration.

If the vapor of phosphoric acid is expelled from the reaction medium by heating and if it is absorbed in sodium hydroxide solution, it causes a serious error. In order to examine this point, two kinds of strong phosphoric acid having the specific gravity 1.93 and 1.96 were used. To the vessel A 5 ml. of the strong phosphoric acid was added and heated at various temperatures for fifteen minutes, while the vapor expelled from the medium was sent by the air stream into a definite amount of 0.1 N sodium hydroxide. From the results shown in Table II it was found that the strong phosphoric acid of the specific gravity 1.93 can not be used for the present

Table II
Effect of the Vaporization of Strong Phosphoric Acid

Specific Gravity of Strong Phosphoric Acid	Temp. °C	0.1 N HCl ml. / 0.1 N NaOH ml.
1.93	Room Temp.	1.000
〃	167	0.989_8
〃	181	0.998_6
〃	200	0.987_9
1.96	Room Temp.	1.000
〃	230	1.000_6
〃	235	1.000_9

purpose and that of the specific gravity 1.96 should be used.

Next, using sodium carbonate as a sample, preliminary experiments were undertaken to examine some conditions. The results obtained are shown in Table III. These experi-

Table III
Determination of Carbon in Sodium Carbonate

Carbon Content Calculated: 11.33%

Sample Weight	Carbon Content		Expelling Time	Remarks
	Found	Deviation		
mg.	%	%	min.	
52.5	10.5	−0.8	15	Without additon of water
55.6	10.6	−0.7	30	
74.7	10.6	−0.7	15	
77.0	11.1	−0.2	30	
52.8	11.2	−0.1	15	With addition of water
55.5	11.3	0.0	15	
57.4	11.3	0.0	13	
66.4	11.4	+0.1	15	
70.5	11.2	−0.1	15	
72.5	11.3	0.0	15	

ments indicated that after the decomposition reaction, the reaction medium should be diluted with water and heated once more to expel the carbon dioxde dissolved in strong phosphoric acid. Also the time required to expel the carbon dioxide present in the apparatus is within fifteen minutes.

Analyses of various known organic compounds, oxalic acid, sodium oxalate, tartaric acid, dulcitol, arabinose, alanine, urea, and methylred were carried out by this method. Thess results are summarized in Table IV. The accuracy of the data is within ±2%. The time required for one analysis is about fifty minutes.

The absorption tube used in this method is very advantageous for the determination of carbon dioxide, because the addition of alkali solution as well as the titration with acid solution can be done under the condition in which carbon dioxide present in the

TABLE IV
DETERMINATION OF CARBON IN ORGANIC COMPOUNDS

Substance	Carbon Content	Sample Weight	Carbon Content	
			Found	Deviation
	%	mg.	%	%
Oxalic Adid $C_2H_2O_4 \cdot 2H_2O$	19.05	40.2	19.2	+0.1
		41.5	19.2	+0.1
		51.1	19.5	+0.4
		57.4	19.1	0.0
		44.2	18.8	−0.3
Sodium Oxalate $Na_2C_2O_4$	17.93	40.3	18.0	+0.1
		44.0	18.0	+0.1
		46.9	18.0	+0.1
		54.2	17.9	0.0
Tartaric Acid $C_4H_4O_5$	32.01	23.1	32.1	+0.1
		25.3	32.1	+0.1
		27.1	32.4	+0.4
		28.2	31.9	−0.1
Dulcitol $C_6H_{14}O_6$	39.56	20.4	39.6	0.0
		21.5	39.6	−0.6
		27.5	39.4	−0.2
		27.5	39.4	−0.2
Arabinose $C_5H_{10}O_5$	40.00	23.5	39.6	−0.4
		24.5	40.0	0.0
		27.3	39.7	−0.3
		32.1	39.6	−0.4
Alanine $C_3H_7O_2N$	38.70	11.7	39.1	+0.4
		15.7	38.5	−0.2
		18.9	38.9	+0.2
		25.6	38.7	0.0
Urea CH_4ON_2	20.00	33.8	20.0	0.0
		35.9	19.8	−0.2
		36.6	20.4	+0.4
		40.8	19.9	−0.1
		47.7	19.9	−0.1
Methylred $C_{15}H_{15}O_2N_3$	66.90	13.4	65.9	−1.0
		14.2	66.4	−0.5
		15.0	66.0	−0.9

atmosphere is excluded perfectly from the titrating system.

For the determination of carbon in organic substances Pregl's dry combustion method has so far been commonly used. However various wet combustion methods have been recently developed to overcome the defects of Pregl's method. Among others the investigations of D. D. Van Slyke and his coworkers[6] are very remarkable. The present method reported by the author is also one of the wet combustion methods for the determination of carbon in organic compounds. As regards the time required for analysis and the accuracy of data the author's method is inferior to that of Van Slyke, but as regards the inexpensiveness of the apparatus and the simplicity of the analytical techniques the former is superior to the latter. The present method can not be applied to volatile compounds. The applicability of the author's method should be further investigated and the improvement of the apparatus is also a problem remaining for the future.

6) e.g., D. D. Van Slyke, *Anal. Chem.*, 26, 1706 (1954).

Summary

(1) A new wet combustion method for the determination of carbon in organic compounds has been developed.

(2) A sample is decomposed by heating with a mixture of potassium iodate and strong phosphoric acid. The liberated carbon dioxide is absorbed in 0.1 N sodium hydroxide, using a spiral type absorber. After adding barium chloride solution the excess sodium hydroxide is titrated with 0.1 N hydrochloric acid, using thymol blue as indicator, in the absorber.

(3) A part of the liberated iodine is absorbed into the tube filled with anhydrous sodium thiosulfate in order to avoid the absorption of the iodine in the alkali solution in the absorber.

(4) Analyses for several organic compounds gave satisfactory results. Using 10 to 60 mg. of samples, the accuracy was within ±2%. Analysis time for one sample is about fifty minutes.

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Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa

Hydrogen Deformation Vibrations[1]

By Ichiro NAKAGAWA and San-ichiro MIZUSHIMA

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Introduction

The normal vibrations of molecules can conveniently be grouped into hydrogen vibrations and skeletal vibrations[2]. Of the former the stretching vibrations are observed in the 3 μ region sufficiently separated from skeletal frequencies, whereas the deformation vibrations appear in a region in which many skeletal vibrations give infrared and Raman frequencies. Therefore, it is desirable to distinguish the hydrogen deformation vibrations from the skeletal vibrations for the interpretation of the vibrational spectra in relation to the structure of molecules[3]. The present calculation has been made with the object of aiding in the assignment of these hydrogen deformation vibrations.

Outline of the Calculation

The calculation was made by Wilson's method[4], according to which we set up a secular equation of the type:

$$|\boldsymbol{GF}-\boldsymbol{E}\lambda| = 0,$$

where $\boldsymbol{G}$ and $\boldsymbol{F}$ are, respectively, the kinetic and the potential energy matrices. In this calculation we consider only that part of a molecule which is directly connected to the CH, CH_2, and CH_3 groups under consideration, because Nakagawa has shown that there is, in general, not much coupling between the hydrogen deformation vibrations and the skeletal vibrations[5]. For example, when we calculate the CH_2 deformation frequencies of CH_3CH_2Cl, we reduce the problem to the vibrations of C–CH_2–Cl.

The symmetry coordinates $\boldsymbol{S}$ obtained from the internal coordinates $\boldsymbol{R}$ by a linear transformation:

$$\boldsymbol{S} = \boldsymbol{UR}$$

are shown in Table I. Here $\boldsymbol{U}$ is an orthogonal matrix, α is a carbon valence angle, and 1, 2, 3, and 4 (subscripts) refer to the four bonds of carbon atom (see Fig. 1). For example, α_{12} denotes the carbon valence angle formed by the first and second bonds. The mode of each hydrogen deformation vibration is understood from the mathematical expression of the corresponding symmetry coordinate shown in Table I[6].

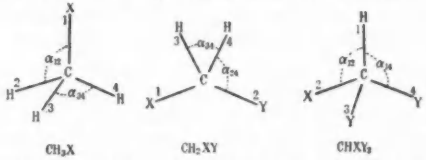


Fig. 1. Internal coordinates of CH_3X, CH_2XY and $CHXY_2$.

TABLE I

SYMMETRY COORDINATES OF HYDROGEN DEFORMATION VIBRATIONS

Molecule	Vibrational mode	Symmetry coordinate
CH_3X	CH_3 degenerate	$\Delta(2\alpha_{34}-\alpha_{23}-\alpha_{24})/\sqrt{6}$ $\Delta(\alpha_{23}-\alpha_{24})/\sqrt{2}$
	CH_3 symmetric	$\Delta(\alpha_{12}+\alpha_{13}+\alpha_{14}-\alpha_{23}-\alpha_{24}-\alpha_{34})/\sqrt{6}$
	CH_3 rocking	$\Delta(2\alpha_{12}-\alpha_{13}-\alpha_{14})/\sqrt{6}$ $\Delta(\alpha_{13}-\alpha_{14})/\sqrt{6}$
CH_2X_2, CH_2XY	CH_2 bending	$\Delta(4\alpha_{34}-\alpha_{13}-\alpha_{14}-\alpha_{23}-\alpha_{24})\sqrt{20}$
	CH_2 wagging	$\Delta(\alpha_{13}+\alpha_{14}-\alpha_{23}-\alpha_{24})/2$
	CH_2 twisting	$\Delta(\alpha_{13}-\alpha_{14}-\alpha_{23}+\alpha_{24})/2$
	CH_2 rocking	$\Delta(\alpha_{13}-\alpha_{14}+\alpha_{23}-\alpha_{24})/2$
CHX_3, $CHXY_2$	CH bending	$\Delta(2\alpha_{12}-\alpha_{13}-\alpha_{14})/\sqrt{6}$ $\Delta(\alpha_{13}-\alpha_{14})/\sqrt{2}$

The matrices $\boldsymbol{G}_S$ and $\boldsymbol{F}_S$ in symmetry coordinates are obtained from the matrices $\boldsymbol{G}_R$ and $\boldsymbol{F}_R$ in internal coordinates through the transformations:

$$\boldsymbol{G}_S = \boldsymbol{UG}_R\boldsymbol{U}'$$
$$\boldsymbol{F}_S = \boldsymbol{UF}_R\boldsymbol{U}'$$

1) A part of this paper was presented at Gordon Research Conference on Infrared Spectroscopy, Meriden, New Hampshire, U.S.A. August, 1954.

2) See, e.g., S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press, New York (1954 ; I. Nakagawa and S. Mizushima, *J. Chem. Phys.*, **21**, 2195 (1953).

3) As to previous researches on hydrogen deformation vibrations, see, e.g., N. Sheppard, *J. Chem. Phys.*, **16**, 690 (1948); **17**, 74 (1949); R.S. Rasmussen, *J. Chem. Phys.*, **16**, 712 (1948).

4) E.B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

5) I. Nakagawa, *J. Chem. Soc. Japan*, **75**, 178, 535 (1954).

6) The modes of these deformation vibrations are shown diagramatically in reference 5.

where U' is the transpose of U.

The diagonal terms G_{SS} of G-matrices are shown in Table II, where μ_C, μ_H, μ_X and μ_Y are the reciprocals of masses of the C, H, X and Y atoms, and r_H, r_C, r_X and r_Y are the reciprocals of the C–H, C–C, C–X and C–Y bond lengths. Furthermore, all the carbon valence angles are assumed to be tetrahedral. The underlined parts of the expressions of G_{SS} are independent of X and Y and contain μ_H which makes the diagonal terms much larger than the cross terms containing the reciprocals of masses of heavier atoms. Therefore, we may neglect the cross terms of G-matrices in the approximate calculation of hydrogen deformation frequencies.

In the case of F-matrices the ratio of diagonal terms to cross terms depends on the nature of the potential function. We used the function of the Urey-Bradley type[7], from which the diagonal terms of F-matrices are calculated as shown in Table II, where

$$J_{HH}=R_H^2(H_{HCH}+2/5F_{H\ldots H}),$$
$$J_{HX}=R_HR_X(H_{HCX}+c_{HX}F_{H\ldots X}).$$

and

$$c_{HX}=tt_1+1/10\,ss_1$$
$$t=(2\sqrt{2}/3)R_X/q_{HX},$$
$$t_1=(2\sqrt{2}/3)R_H/q_{HX},$$
$$s=(1/q_{HX})(R_H+1/3\,R_X),$$
$$s_1=(1/q_{HX})(R_X+1/3\,R_H),$$
$$q_{HX}=(R_H^2+R_X^2+2/3\,R_HR_X)^{\frac{1}{2}}.$$

Here H_{HCH} and H_{HCX} are force constants for the deformation of the HCH and HCX angles, $F_{H\ldots H}$ and $F_{H\ldots X}$ those for the changes of distances between the two nonbonded H atoms and between the nonbonded H and X atoms, R_H and R_X the C–H and C–X bond lengths, and k's the intramolecular tensions[7]. The values of force constants and intramolecular tensions are shown in Table III[2,8].

7) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

8) See also T. Shimanouchi, *J. Chem. Soc. Japan*, **74**, 266 (1953); I. Nakagawa and S. Mizushima, *J. Chem. Phys.*, **22**, 759 (1954); I. Nakagawa, *J. Chem. Soc. Japan*, **76**, 540 (1955).

TABLE II

DIAGONAL TERMS OF G- AND F-MATRICES, G_{SS} AND F_{SS}

Molecule	Vibrational mode	G_{SS}	F_{SS}
CH_3X	CH_3 degenerate	$\underline{[(5/2)\mu_H+(8/3)\mu_C]r_H^2}$	$J_{HH}+(1/2\sqrt{2})k_1$
	CH_3 symmetric	$\underline{[2\mu_H+(16/3)\mu_C]r_H^2}$	$(1/2)(J_{HH}+J_{HX})+(3/2\sqrt{2})k_1$
	CH_3 rocking	$\underline{[\mu_H+(1/6)\mu_C]r_H^2}+(3/2)\mu_Xr_X^2+\mu_C[(3/2)\times r_X^2+r_Hr_X]$	$J_{HX}+(1/2\sqrt{2})k_1$
CH_2X_2	CH_2 bending	$\underline{[(5/2)\mu_H+(10/3)\mu_C]r_H^2}+(1/10)\mu_Xr_X^2+(2/15)\mu_Cr_X^2-(4/3)\mu_Cr_Hr_X$	$(4/5)J_{HH}+(1/5)J_{HX}+(3/10\sqrt{2})k_2$
	CH_2 wagging	$\underline{[(3/2)\mu_H+3\mu_C]r_H^2}+(1/2)\mu_Xr_X^2+\mu_C[(1/3)r_X^2+2r_Hr_X]$	$J_{HX}+(3/2\sqrt{2})k_2$
	CH_2 twisting	$\underline{(3/2)\mu_Hr_H^2}+(3/2)\mu_Xr_X^2$	$J_{HX}-(1/2\sqrt{2})k_2$
	CH_2 rocking	$\underline{[(1/2)\mu_H+(1/3)\mu_C]r_H^2}+(3/2)\mu_Xr_X^2+\mu_C(3r_X^2+2r_Hr_X)$	$J_{HX}+(3/2\sqrt{2})k_2$
CH_2XY	CH_2 bending	$\underline{[(5/2)\mu_H+(10/3)\mu_C]r_H^2}+(1/20)(\mu_Xr_X^2+\mu_Yr_Y^2)+(1/20)\mu_C(r_X^2+r_Y^2)+(1/30)\mu_Cr_Xr_Y-(2/3)\mu_C(r_Hr_X+r_Hr_Y)$	$(4/5)J_{HH}+(1/10)(J_{HX}+J_{HY})+(3/10\sqrt{2})k_2$
	CH_2 wagging	$\underline{[(3/2)\mu_H+3\mu_C]r_H^2}+(1/4)(\mu_Xr_X^2+\mu_Yr_Y^2)+(1/4)\mu_C(r_X^2+r_Y^2)-(1/6)\mu_Cr_Xr_Y+\mu_C(r_Hr_X+r_Hr_Y)$	$(1/2)(J_{HX}+J_{HY})+(3/2\sqrt{2})k_2$

Molecule	Vibrational mode	G_{SS}	F_{SS}
	CH_2 twisting	$(3/2)\mu_H r_H^2+(3/4)(\mu_X r_X^2+\mu_Y r_Y^2)$ $+(3/4)\mu_C(r_X^2+r_Y^2)-(3/2)\mu_C r_X r_Y$	$(1/2)(J_{HX}+J_{HY})-(1/2\sqrt{2})k_2$
	CH_2 rocking	$[(1/2)\mu_H+(1/3)\mu_C]r_H^2+(3/4)(\mu_X r_X^2+\mu_Y r_Y^2)$ $+(3/4)\mu_C(r_X^2+r_Y^2)+(3/2)\mu_C r_X r_Y$ $+\mu_C(r_H r_X+r_H r_Y)$	$(1/2)(J_{HX}+J_{HY})+(3/2\sqrt{2})k_2$
CHX_3	CH bending	$[(3/2)\mu_H+(3/2)\mu_C]r_H^2+\mu_X r_X^2+\mu_C[(1/6)r_X^2$ $+r_H r_Y]$	$J_{HX}+(1/2\sqrt{2})k_3$
$CHXY_2$	CH bending (A′)	$[(3/2)\mu_H+(3/2)\mu_C]r_H^2+(2/3)\mu_X r_X^2$ $+(1/3)\mu_Y r_Y^2+\mu_C[(2/3)r_H r_X$ $+(1/3)r_H r_Y+(2/3)r_X^2-(10/9)r_X r_Y$ $+(11/18)r_Y^2]$	$(2/3)J_{HX}+(1/3)J_{HY}+(1/2\sqrt{2})k_3$
	CH bending (A″)	$[(3/2)\mu_H+(3/2)\mu_C]r_H^2+\mu_Y r_Y^2+\mu_C[(1/6)r_Y^2$ $+r_H r_Y]$	$J_{HY}+(1/2\sqrt{2})k_3$
CH_3–CH_3*	CH_3 degenerate	$(G_{SS})_0$	$J_{HH}+(1/2\sqrt{2})k_1$
	CH_3 symmetric	$(G_{SS})_0$	$(1/2)(J_{HH}+J_{HC})+(3/2\sqrt{2})k_1$
	CH_3 rocking	$(G_{SS})_0\pm\mu_C(3r_C^2+r_C r_H)\cos\theta$	$J_{HC}+(1/2\sqrt{2})k_1$
XCH_2 –CH_2X**	CH_2 bending	$(G_{SS})_0\pm[-2\mu_C\{(2/3)r_C r_H-(1/10)r_C^2$ $-(1/30)r_C r_X\}\cos\theta]$	$(4/5)J_{HH}+(1/10)(J_{HX}+J_{HC})$ $+(3/10\sqrt{2})k_2$
	CH_2 wagging	$(G_{SS})_0\pm(1/2)\mu_C[r_C^2+2r_C r_H-(1/3)r_C r_X]\cos\theta$	$(1/2)(J_{HX}+J_{HC})+(3/2\sqrt{2})k_2$
	CH_2 twisting	$(G_{SS})_0\pm[-(3/2)\mu_C(r_C^2-r_C r_X)\cos\theta]$	$(1/2)(J_{HX}+J_{HC})-(1/2\sqrt{2})k_2$
	CH_2 rocking	$(G_{SS})_0\pm[-(3/2)\mu_C\{r_C^2+r_C r_X$ $+(2/3)r_C r_H\}\cos\theta]$	$(1/2)(J_{HX}+J_{HC})+(3/2\sqrt{2})k_2$

* $(G_{SS})_0$ signifies G_{SS} of CH_3X for X=C. The signs+and−refer, respectively, to the symmetric (A) and the anti-symmetric (B) vibrations to the C_2 axis. The azimuthal angle θ is taken as zero for the trans position.

** $(G_{SS})_0$ signifies G_{SS} of CH_2XY for Y=C.

TABLE III

VALUES OF FORCE CONSTANTS H AND F IN 10^5 dyn./cm. AND INTRAMOLECULAR TENSION k IN 10^{-11} dyn. cm.

Deformation constant H		Repulsion constant F		Intramolecular tension k							
H–C–H	0.40	H..(C)..H	0.10							CH_4	0.00
H–C–F	0.06	H..(C)..F	1.15	CH_3F	0.10	CH_2F_2	0.20	CHF_3	0.35	CF_4	0.45
H–C–Cl	0.05	H..(C)..Cl	0.80	CH_3Cl	0.05	CH_2Cl_2	0.10	$CHCl_3$	0.20	CCl_4	0.26
H–C–Br	0.04	H..(C)..Br	0.65	CH_3Br	0.03	CH_2Br_2	0.07	$CHBr_3$	0.15	CBr_4	0.25
H–C–I	0.04	H..(C)..I	0.52	CH_3I	0.02	CH_2I_2	0.04	CHI_3	0.10		
H–C–CX_3	0.15	H..(C)..CX_3	0.40	CH_3CX_3	0.05						
H–C–CH_3	0.25	H..(C)..CH_3	0.50					$CH(CH_3)_3$	0.03	$C(CH_3)_4$	0.04
H–C–C(≡)	0.21	H..(C)..C(≡)	0.50	CH_3CN	0.04	$CH_2(CN)_2$	0.07				
H–C–N	0.20	H..(C)..N	0.60	CH_3NC	0.05						

Although the diagonal terms of F-matrices are not always large as compared with the cross terms, approximate calculations of hydrogen deformation frequencies have been made from the product $G_{ss}F_{ss}$ of the diagonal terms shown in Table II. The difference between the computed and the observed frequencies has been found to be less than 5%[9].

In the higher approximations we have taken into account the effect of the cross terms in the following form:

$$(GF)_{ss}=G_{ss}F_{ss}+a,$$
$$\lambda=(GF)_{ss}+b,$$

where a and b are the correction terms[9].

Results for CH Deformation Frequencies

The calculations have been made for many molecules, including those of methane and ethane derivatives and their deuterated compounds. The computed values have been shown to be in good agreement with those observed[10]. The frequency ranges of hydrogen deformation vibrations thus obtained are shown in Table IV, where those of fluorine compounds have been omitted, because they show abnormal values[10].

The inspection of the expressions of G_{ss} and F_{ss} shown in Table II, together with the numerical values given in Table IV, gives us information on the specific features of hydrogen deformation vibrations, which are useful in the assignment of these vibrations. Some of these features are listed in the following:

(1) The CH_3 degenerate deformation vibrations and the CH_2 bending vibrations appear in narrow frequency regions. Furthermore, these regions are separated from those of other hydrogen deformation vibrations.

(2) The CH_3 symmetric deformation vibrations also appear in a narrow frequency range, when this group is directly connected to a carbon atom as CH_3–C–.

(3) The frequency values of the hydrogen deformation vibrations in the same series (e.g. CH_3X, CH_2X_2 and CHX_3) decrease in the following order: CH_3 degenerate deformation $>CH_2$ bending$>CH_3$ symmetric deformation $>CH_2$ wagging$>$CH bending$>CH_2$ twisting $>CH_3$ rocking $>CH_2$ rocking. In some cases

TABLE IV

THE FREQUENCY RANGES OF HYDROGEN DEFORMATION VIBRATIONS IN cm^{-1}

Molecule*	Vibrational mode	Frequency range
CH_3X	CH_3 degenerate	ca. 1450
	CH_3 symmetric	1250–1400
	CH_3 rocking	900–1150
CH_2X_2 & CH_2XY	CH_2 bending	1350–1450
	CH_2 wagging	1100–1350
	CH_2 twisting	1000–1300
	CH_2 rocking	700–1000
CHX_3 & $CHXY_2$	CH bending	1100–1350
CH_3CX_3	CH_3 degenerate	ca. 1450
	CH_3 symmetric	1370–1390
	CH_3 rocking	1000–1100
CH_3CHX_2 & CH_3CH_2X	CH_3 degenerate (A' & A'')	ca. 1450
	CH_3 symmetric	1370–1390
	CH_3 rocking (A' & A'')	1000–1100
CH_3COX	CH_3 degenerate (A' & A'')	ca. 1420
	CH_3 symmetric	ca. 1360
	CH_3 rocking (A' & A'')	1000–1100
$(CH_3)_2CHX$	CH_3 degenerate (A' & A'')	ca. 1450
	CH_3 symmetric (A' & A'')	1370–1390
	CH_3 rocking (A' & A'')**	900–1150
	C–C stretching**	870–890 (A'), 1120–1140 (A'')
	CH bending	variable (A'), 1320–1340 (A'')
$(CH_3)_3CX$	CH_3 degenerate (A_1 & E)	ca. 1450
	CH_3 symmetric (A_1 & E)	1370–1390
	CH_3 rocking (A_1 & E)**	900–1150
	C–C stretching (A_1 & E)**	800–810 (A_1), 1220–1240 (E)
XCH_2CH_2X	CH_2 bending	1400–1450
	CH_2 wagging	1150–1350
	CH_2 twisting	1000–1300
	CH_2 rocking	700–1000 ($B_g > A > B > A_u$)

* Fluorine compounds are excluded.

** The C–C stretching and CH_3 rocking vibrations are coupled with each other considerably in these cases.

9) I. Nakagawa, *J. Chem. Soc. Japan*, **75**, 1259 (1954).

10) I. Nakagawa, ibid., **76**, 540 (1955).

the order of the CH_2 wagging frequency and the CH_3 symmetric deformation frequency may be reversed.

(4) The CH bending frequencies of CHX_3 and CHY_3, which are degenerate, are split into two frequencies A' and A'' in $CHXY_2$ where A'' has nearly the same frequency as the degenerate frequency of CHY_3 and A' has a value lying between those of CHX_3 and CHY_3 but closer to that of CHX_3.

(5) According to the result of the similar calculation made for molecules of the type, XH_2C-CH_2X, the two deformation frequencies, one symmetric and the other antisymmetric to the C_2 axis, are not much different from each other and are not sensitive to the change of azimuthal angle of the internal rotation about the C-C axis, except for the CH_2 rocking frequencies. Furthermore, the selection rules for the rocking frequencies are quite different for the trans, gauche and cis forms. The frequency values of the rocking vibrations decrease in the following order: $B_g(trans) > A(gauche) > B(gauche) > A_u(trans)$. The observation of rocking frequencies provides important experimental data of the optical isomerism of a new type described in previous notes[11].

NH_3-Deformation Frequencies in Ammine Complexes

When the NH_3 group is coordinated about a central metal atom in coordination complexes such as $[Co(NH_3)_6]Cl_3$, we expect the appearance of three deformation frequencies similar to those of the CH_3 deformation frequencies. Actually we have found in these complexes three frequencies at about 1610, 1330 and 830 cm^{-1} and these are assigned, respectively, to the degenerate deformation, symmetric deformation and rocking vibrations as shown in a previous paper[12]. There we did not describe the procedure of the calculation at all, but it is easily seen that this is quite similar to that of the calculation of CH_3 deformation vibrations of CH_3X shown in Table I. The force constants used in this calculation are shown in Table V.

It is to be noted that of these five constants H_{HNH}, $F_{H\cdots(N)\cdots H}$ and k can also be used for the calculation of the normal frequencies of ammonia, NH_3, ammonium ion, NH_4^+ and their deuteration products, ND_3 and ND_4^+. Therefore, the reasonableness of their values can be checked by the normal frequency calculations for these compounds and ions. As shown in Table VI the calculated values are in good agreement with the observed values and consequently, these constants are concluded to have reasonable values.

TABLE V

THE VALUES OF FORCE CONSTANTS H AND F IN 10^5 DYNES/CM. AND INTRAMOLECULAR TENSION k IN 10^{-11} dyn. cm.

H		F		k
H-N-H	0.54	H..(N)..H	0.06	−0.04
H-N-Co	0.18	H..(N)..Co	0.10	

TABLE VI*

CALCULATED AND OBSERVED FREQUENCIES IN cm^{-1} OF NH_3, ND_3, NH_4^+ AND ND_4^+

	NH_3		ND_3	
	Calc.	Obs.	Calc.	Obs.
A_1	3333	3336	2374	2419
	951	950	724	749
E	3410	3414	2506	2555
	1630	1628	1188	1191
	NH_4^+		ND_4^+	
	Calc.	Obs.	Calc.	Obs.
A_1	3041	3041	2150	2214
E	1710	1710	1209	1215
T	3138	3138	2321	2350
	1403	1403	1049	1066

* Evidently for the calculation of these frequencies the N-H stretching force constants (6.30×10^5 dynes/cm. for NH_3 and 5.26×10^5 dynes/cm. for NH_4^+) are needed in addition to the three constants mentioned above.

Using the force constants shown in Table V, the frequencies of the NH_3 degenerate deformation, symmetric deformation and rocking vibrations of $[Co(NH_3)_6]Cl_3$ have been calculated and compared with the observed values in Table VII. The agreement between the computed and observed values is good and consequently our assign-

TABLE VII

CALCULATED AND OBSERVED DEFORMATION FREQUENCIES IN cm^{-1} OF THE NH_3 AND ND_3 LIGANDS

Vibrational mode	$[Co(NH_3)_6]Cl_3$		$[Co(ND_3)_6]Cl_3$	
	Calc.	Obs.	Calc.	Obs.
Degenerate	1579	1610	1156	1162
Symmetric	1340	1330	1021	1024
Rocking	854	835	628	outside the NaCl region

11) J.V. Quagliano and S. Mizushima, *J. Am. Chem. Soc.*, 75, 6084 (1953). See also S. Mizushima, I. Nakagawa, I. Ichishima and T. Miyazawa, *J. Chem. Phys.*, 22, 1614 (1954).

12) S. Mizushima, I. Nakagawa and J.V. Quagliano, *J. Chem. Phys.*, 23, 1367 (1955).

ment has been shown to be correct. Furthermore, this assignment has been checked by observing the isotopic shift of these frequencies[12]. As shown in the same table, the observed frequencies of the deformation vibrations of the ND_3 ligand are in good agreement with those calculated from the isotopic relations.

Some authors have explained these bands as arising from the metal-ligand vibrations of the octahedral cation[13]. However, from our calculation it has been shown that the assignment made in this paper is more reasonable.

From the result of the present research we can conclude that the metal-to-ligand bond should be fairly covalent in metal ammine complexes. If this bond were ionic, we could conclude that there are no rocking vibrations of the NH_3 group.

13) H.G. Hill and A.F. Rosenberg, *J. Chem. Phys.*, 22, 148 (1954).

Summary

The CH, CH_2 and CH_3 deformation frequencies in various organic compounds and the NH_3 deformation frequencies in metal ammine complexes have been calculated based on the Urey-Bradley field. The fact that diagonal terms of G-matrices for these vibrations are much larger than the cross terms makes the approximate calculation quite easy. The frequency range of each of these vibrations has been tabulated and their specific features have been pointed out, which will aid in the assignment of the frequencies observed for many organic compounds and metal ammine complexes.

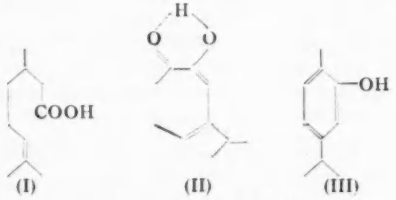
Chemical Laboratory, Faculty of Science,
The University, of Tokyo,
Tokyo

*The Structure of Chamenol**

By Tetsuo NOZOE, Yoshio KITAHARA, and Tomio ARAI

(Received May 18, 1955)

Some time ago, Nozoe and others[1] isolated two different phenolic substances from the acid portion of the essential oil of *Chamaecyparis taiwanensis Masamune et Suzuki*, together with *l*-rhodinic acid (I) and hinokitiol (II) (or β-thujaplicin), and designated the phenolic substances chamenol-A (oil) and chamenol-B (m.p. 41–42°, b.p. 122–124°/15 mmHg, $C_9H_{12}O_2$ or $C_{10}H_{14}O_2$). Later studies by Nozoe and others[2] revealed that chamenol-A is carvacrol (III).



(I) (II) (III)

By studies[2] on the acid portion of *Thujopsis dolabrata Sieb. et Zucc.*, *l*-rhodinic acid (I), hinokitiol (II) and carvacrol (III) were isolated; however the fraction (b.p. 122–125°/15 mmHg) that seemed to be chamenol-B, on seeding with crystals of chamenol-B, afforded crystals of α-thujaplicin, and chamenol-B could not be isolated from the essential oil of *Thujopsis*. Luckily, however, a minute amount of chamenol-B was brought back to Japan on repatriation from Formosa and its structural studies were again carried out.

Since chamenol-A has been found to be identical with carvacrol, chamenol-B will henceforth be referred to simply as *chamenol*.

The infrared spectra[3] (Figs. 1 and 2) of chamenol point to the presence of the following groups[4].

2.80 μ: hydroxyl group
3.24 μ (shoulder): probably C-H of benzene nucleus
3.37 and 3.45 μ: aliphatic C-H
6.24 and 6.60 μ: benzene nucleus
6.87, 7.32, 8.52 and 8.72 μ: isopropyl group[5]

* This work was presented at the XIIIth International Congress of Pure and Applied Chemistry at Stockholm, July 31st, 1953.

1) T. Nozoe, *Science of Drugs*, 3, 174 (1949); *Science Repts. Tohoku Univ., First Ser.*, 34, 199 (1950).

2) T. Nozoe, A. Yasue and K. Yamane, *Proc. Japan Acad.*, 27, 15 (1951).

3) Infrared absorption spectrum was measured by Dr. M. Tsuboi of Faculty of Science, Tokyo University.

4) a) H.W. Thompson, *J. Chem. Soc.*, 328 (1948).
b) N.B. Colthup, *J. Optical Soc. Am.*, 40, 397 (1950).
c) H.M. Randall, R.G. Fowler, N. Fuson and J.R. Dangl, *Infrared Determination of Organic Structures*. D. Van Nostrand Co., N.Y. (1949).

5) D.M. Simpson and G.B.B.M. Sutherland, *Proc. Roy. Soc.* (London), A 199, 169 (1949); *Chem. Abstr.*, 44, 2372 (1950).

8.05 and 8.85 μ: aromatic ether (the absorption band due to C-O-C in trimethoxybenzaldehyde is at 8.87 μ[4c])

11.43 and 12.49 μ: 1, 2, 4-trisubstituted benzene.

The fact that the 5.5–6.1 μ region lacks any absorption clearly shows that the molecule does not contain any carbonyl function.

Analytical values of chamenol correspond to the formula $C_{10}H_{14}O_2$, containing one methoxyl group. It is a phenolic substance and colors deep green with ferric chloride but did not give a red color in organic solvents (chloroform or benzene), characteristic of tropolones. It gives a monobenzoate, m.p. 64–65° and a *p*-nitrobenzoate, m.p. 87°. Chamenol shows a blue green coloration by the Liebermann reaction[6] and therefore the para-position of the phenol is apparently free of a substituent.

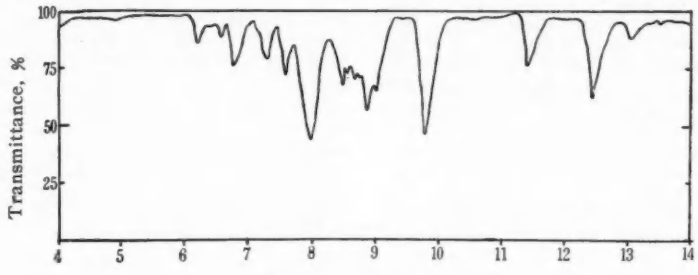


Fig. 1. Infrared absorption spectrum of chamenol (solid).

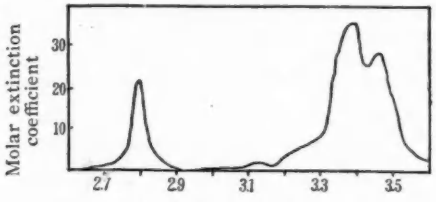


Fig. 2. Near infrared absorption spectrum of chamenol in 0.01 mol./l. CCl_4 solution.

From the analytical results and infrared determination, chamenol may be assumed to be a phenol possessing a methoxyl and an isopropyl group. The ultraviolet spectrum of chamenol, as shown in Fig. 3, possesses an absorption maximum at 281 mμ while the maximum of dihydroeugenol is 281 mμ.

These results suggest that chamenol is an isopropyl derivative of guaiacol and could reasonably be represented by structure (IV).

Based on this surmise, the synthesis of (IV) was initiated from 2-bromo-4-isopropylanisole (V), obtained from *p*-isopropylphenol[7]. The bromide (V) was converted to the Grignard reagent in the presence of isopropyl bromide and followed by oxidation with oxygen to afforded 5-isopropylguaiacol, m.p. 41-42°. Both this substance and its *p*-nitrobenzoate showed no depression of the melting points on admixture with chamenol and its *p*-nitrobenzoate respectively; thus the structure of chamenol was confirmed as (IV).

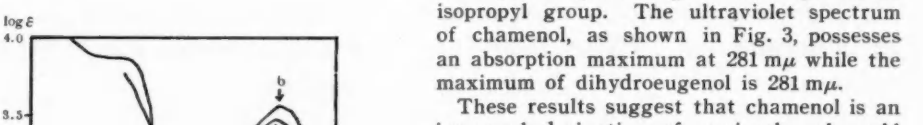
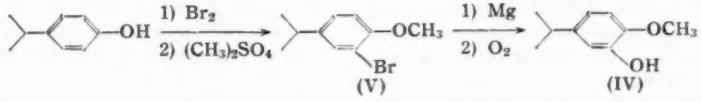


Fig. 3. Ultraviolet absorption spectra in methanol.
a) chamenol b) dihydroeugenol



6) C. Liebermann, *Ber.*, **7**, 806, 1098 (1874); W.B. Deichmann, *Ind. Eng. Chem. Anal. Ed.*, **16**, 37 (1944).

7) R.A. Smith, *J. Am. Chem. Soc.*, **56**, 718 (1934).

Experimental

Chamenol[1]—Colorless scales from petroleum ether, b.p. 122–124°/15 mmHg, m.p. 41–42°. Anal. Found: C, 72.44; H, 8.31; Mol. wt. (Rast method), 169; OCH_3 (by Zeisel method), 18.01. Calcd. for $C_{10}H_{14}O_2$: C, 72.44; H, 8.48; Mol. wt., 166; OCH_3, 18.67. *p-Nitrobenzoate*: Pale yellow prisms from ethanol, m.p. 86–87°. Anal. Found: C, 64.42; H, 5.46; N, 4.65. Calcd. for $C_{17}H_{17}O_5N$: C, 64.76; H, 5.40; N, 4.44. *Benzoate*: Colorless scales from ethanol, m.p. 64–65°. Anal. Found: C, 75.24; H, 6.95. Calcd. for $C_{17}H_{18}O_2$: C, 75.53; H, 6.71.

2-Bromo-4-isopropylphenol—To a solution of 12 g. of 4-isopropylphenol[7] in 40 cc. of chloroform, 17 cc. of chloroform containing 14 g. of bromine was added under ice-cooling. Removal of the solvent followed by distillation furnished monobromo compound (15.7 g., 83%), b.p. 119–120°/15 mmHg. *p-Nitrobenzoate*: Colorless prisms from ethanol, m.p. 83–84°. Anal. Found: N, 4.08. Calcd. for $C_{16}H_{14}O_4NBr$: N, 3.87.

2-Bromo-4-isopropylanisole (V)—To a stirred mixture of 16.5 g. of 2-bromo-4-isopropylphenol, and 6 g. of sodium hydroxide in 30 cc. of water, 10.5 g. of dimethyl sulfate was added dropwise, the reaction mixture was heated at 60–70° for five hours after the last addition, and extracted by ether. Removal of the solvent from the extract followed by distillation furnished the anisole (V, 11.9 g., 68%), b.p. 113–116°/1 mmHg. Anal. Found: C, 52.38; H, 5.53. Calcd. for $C_{10}H_{13}OBr$: C, 52-42; H, 5.72.

5-Isopropylguaiacol (IV)—Grignard reagent prepared from 4 g. of (V), 3.2 g. of isopropyl bromide, and 1 g. of activated magnesium was oxidized by the introduction of dry oxygen for four hours. After standing for fifteen hours, the reaction mixture was refluxed with dilute sulfuric acid for one hour. The ethereal layer was extracted with 20 cc. of 5% sodium hydroxide solution and the alkali layer was acidified and extracted with ether. Removal of the solvent from dried ether solution followed by distillation furnished colorless solid (1.1 g. 38%, b.p. 115–124°/10 mmHg, m.p. 38–40°), which after recrystallization from petroleum ether, afforded colorless scales, m.p. 41–42°, 5-isopropylguaiacol (IV). (IV) and its derivatives (*benzoate*, m.p. 64–65°, *p-nitrobenzoate*, m.p. 86–87°) were respectively found by admixture to be identical with chamenol and its derivatives.

Summary

The structure of chamenol, a phenolic substance isolated from the acid fraction of the essential oil of *Chamaecyparis taiwanensis*, was proved to be 2-methoxy-5-isopropylphenol.

Chemical Institute, Faculty of Science, Tohoku University, Sendai

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Cathodo-luminescence of Samarium as Applied to the Structural Studies of Alumina. I. Three Prototypes for the Luminescence Spectra of Samarium in Alumina

By Eiichi IWASE

(Received April 25, 1955)

Introduction

Studies on the structures of alumina and alumina-hydrate as well as their structural variations during dehydration and calcination have made steady and marked progress in recent years, being based mainly on the results of X-ray diffraction investigations. The present author has carried out over a number of years extensive investigations on the cathodo-luminescence spectra of certain rare earths, such as praseodymium and samarium, which were impregnated into a great variety of anhydrous alumina, derived from hydrargillite, bayerite and boehmite, or from hydrous alumina gels, or from hydrated crystals of aluminium salts.

Rohden[1] as well as the present author[2] have already made spectrographic studies on the cathodo-luminescence of samarium imbedded in alumina and a different set of luminescence bands was assigned for it respectively. These two sets of the luminescence spectra for the samarium-bearing alumina are likely to correspond to an observation described in Lecoq de Boisbaudran's[3] classical work; namely the samarium imbedded in alumina gave two different cathodo-luminescence spectra, according as the calcination temperature was varied.

1) Ch. de Rohden, *Ann. chim.*, [9] **3**, 362 (1915).
2) E. Iwase, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **34**, 770 (1938).
3) Lecoq de Boisbaudran, *Compt. rend.*, **105**, 258 (1887).

Rohden[4] proposed, on the other hand, one definite kind of cathodo-luminescence spectrum for praseodymium-bearing alumina. Three prototypes have, however, been brought forward quite recently by the present author and his collaborators[5] for cathodo-luminescence spectra of the praseodymium imbedded in various kinds of alumina, and some interpretations have also been given for their occurrences from a structural standpoint.

This paper presents three prototypes of the cathodo-luminescence spectra owing to samarium existing in three different kinds of alumina respectively, and shows the interdependence of the alumina-structure and the samarium-luminescence spectrum, since cathodo-luminescence bands due to the samarium ions are, in general, much more intense than those due to the praseodymium ions in solid inorganic ground-materials.

TABLE I

CATHODO-LUMINESCENCE SPECTRA OF SAMARIUM-BEARING ALUMINA

Prototype I		Prototype II		Prototype III	
Wave-length (mμ)	Intensity	Wave-length (mμ)	Intensity	Wave-length (mμ)	Intensity
656		661		656	
651	w	658.5	w	654	w
646 (maximum)	s	650		649.5	w
644		648	ww	644.5	w
635	w	644.5		625	
		642	ww	623	s
		637		621.5	
		635	ww	620	s
621		624.5		616	
		623	s	615	m
		622		613	
		620.5	m	612	s
		619		611	
	m	616.5	ss	609.5	s
		614.5		609	
		612	w	607	s
		610	s	606	
		608.5	m	604	m
		606.5			
604		604.5		603	
		602	ww	602	m
599.5 (maximum)	ss	600	ww	600	
		596		598	w
		595		596.5	ss
594		593.5	m	593	w
		591			
		590	m	589.5	
		590			
		589	m		ww
	w	588.5	s		
		587		587	
		586	ww		
		585	ww	583.5	
		582.5		582.5	w
581		581		581	
		580	s	580	w
		578		578	
		576.5	ww	577	ww
		575			
		573.5	ww		
574		572	w	571.5	m
	s			568	ww
568				566	ww
567	ww			562.5	m
565				561	m
560.5	m			553.5	ww
551				548.5	ww
547	w				
545	w			542.5	ww
542.5					
541	m				
540.5	ww				

4) Ch. de Rohden, *Ann. chim.*, [9] **3**, 360 (1915).

5) E. Iwase, S. Nishiyama and T. Isono, This Bulletin, **28**, 345 (1955).

Experimental

Three samples of samarium-bearing alumina were prepared by the following methods.

Sample 1: The hydrous alumina gel was precipitated by the addition of ammonia to a cold solution of aluminium sulphate. After being washed with water and dried at 110°C, the gel was soaked with a solution of samarium nitrate and then ignited at about 900°C for one hour.

Sample 2: Crystals of aluminium nitrate enneahydrate were partially calcined at about 180°C until they became porous masses, which were ground to fine powders, soaked with the solution of samarium nitrate and roasted at 1200°C or above.

Sample 3: Fine granular crystals of the hydrargillite obtained by the Bayer process, namely crystals of alumina-trihydrate, were previously calcined at a suitable temperature, for example 800°C for one hour. The anhydrous alumina thus obtained was, after the solution of samarium nitrate had been added, ignited at about 900°C for one hour.

The samarium introduced into the above-mentioned samples of alumina, serves as an activator to cause the cathodo-luminescence, and its concentration was adjusted to be nearly 1% calculated as oxide for a ground-material, namely alumina in the present cases.

These samples of samarium-bearing alumina were subjected to cathode-ray bombardment in a small Urbain tube and their luminescence was spectrographically investigated by employing a Feuss glass-prism spectrograph.

Results

Table I shows results of the cathodo-luminescence spectra given by the samples 1, 2 and 3. Relative intensities of the luminescence bands were estimated visually and indicated by the following symbols; ss(very strong), s(strong), m(medium), w(weak) and ww(very weak).

These luminescence spectra are reproduced in Photos. 1, 2 and 3. They are schematically given in Fig. 1, (a), (b) and (c) in order to facilitate comparisons. Luminescence spectra of the samples 1, 2 and 3 have quite different and readily distinguishable appearances, and thus may be designated as the three prototypes I, II and III respectively for the cathodo-luminescence spectra due to the samarium ions, which have been imbedded in different modifications of alumina. The prototype I of samarium-luminescence spectrum is composed of several broad diffuse bands, while the prototypes II and III are composed of a number of relatively sharp line-like bands.

Discussion

The sample 1 of samarium-bearing alumina is found, on one hand, giving the cathodo-luminescence spectrum of the prototype I (Fig. 1, a, and Photo. 1) and, on the other

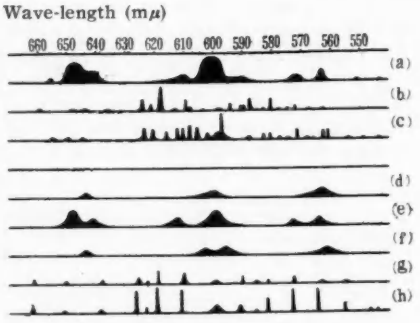

Fig. 1. Schematic representation of luminescence spectra due to samarium in alumina and in water.

Cathodo-luminescence spectrum of prototype I (a), of prototype II (b), and of prototype III (c), Luminescence spectrum of Al_2O_3-Sm calcined at low temperatures (Lecoq de Boisbaudran) (d), of Al_2O_3-Sm (Iwase) (e), of aqueous solution of $SmCl_3$ (Lecoq de Boisbaudran) (f), of Al_2O_3-Sm calcined at elevated temperatures (Lecoq de Boisbaudran) (g), and of Al_2O_3-Sm (Rohden) (h).

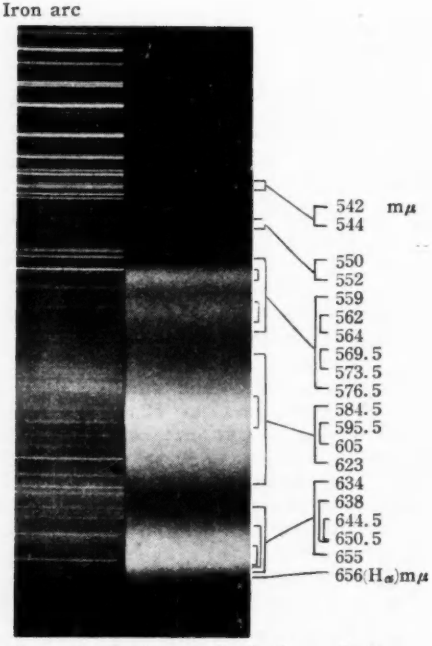

Photo. 1. Prototype I of the cathodo-luminescence spectrum of samarium-bearing alumina.

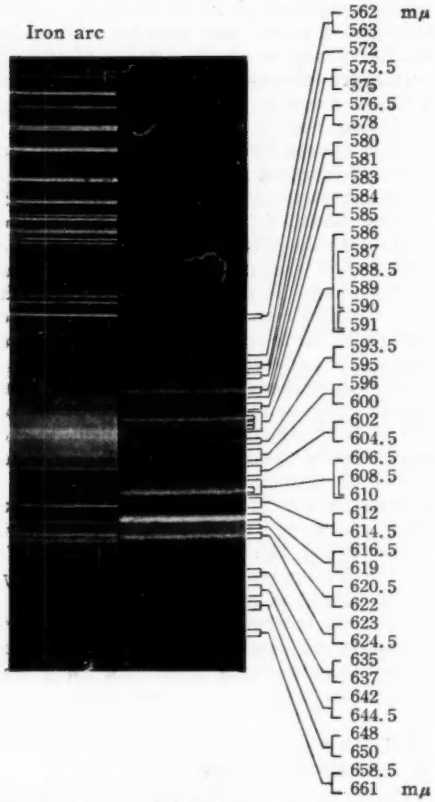

Photo. 2. Prototype II of the cathodo-luminescence spectrum of samarium-bearing alumina.

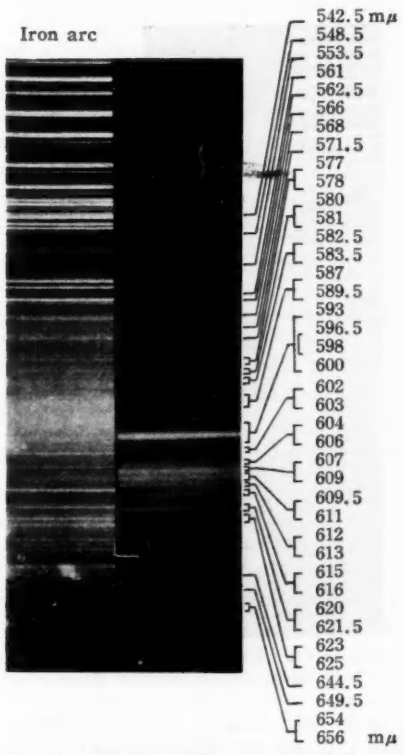

Photo. 3. Prototype III of the cathodo-luminescence spectrum of samarium-bearing alumina.

hand, having the structure of γ-modification as revealed by an X-ray investigation[5]. This luminescence prototype may simply accounted for by the luminescence spectrum caused by the excitation of samarium ions in solution, since the present author has confirmed that samarium ions distributing at random in an optically isotropic substance, for example in an ordinary glass, show a cathodo-luminescence spectrum quite akin to that of the prototype I (Photo. 4). The γ-modification of alumina is considered to be, in harmony with the above statement, constructed from the oxygen-ion network of cubic close-packing with aluminium ions distributing in a statistical way over its whole interstices evenly[5].

Additional examples for this luminescence prototype are supplied by samarium-bearing alumina prepared by means of the calcination at low temperatures, as already described by Lecoq de Boisbaudran[3] (Fig. 1, d) as well as the present author[2] (Fig. 1, e), and by a solution of samarium chloride, as shown by Lecoq de Boisbaudran[3] (Fig. 1, f).

The luminescence spectrum of the prototype II (Fig. 1, b and Photo. 2) is decisively produced by samarium ions imbedded in a corundum structure, in which oxygen ions are arranged in hexagonal close-packing, because a study of the X-ray diffraction pattern has revealed that the sample 2 is really α-modification of alumina[5]. The cathodo-luminescence spectrum of samarium-bearing alumina calcined at greatly elevated temperatures belongs to this prototype, according to observations by Lecoq de Boisbaudran[3] (Fig. 1, g) and Rohden[1] (Fig. 1, h).

In addition to the above-mentioned two luminescence prototypes another conspicuous luminescence spectrum is obtained, which seems overlooked by the investigators. This new luminescence spectrum may be designated as the prototype III for the luminescence spectrum of samarium ions existing in an

6) E. J. W. Verwey, *Z. Krist.*, 91, 68 (1935).

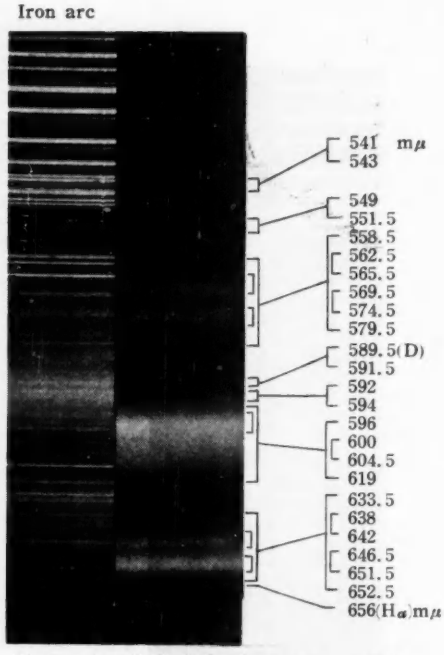

Photo. 4. Cathodo-luminescence spectrum of samarium-bearing glass.

alumina, and is seen in its pure form only with a sample of samarium-bearing alumina, which has been yielded from the hydrargillite by a suitable heat treatment, prior to the addition of samarium (Fig. 1, c and Photo. 3). Brown[7] and Day[8] have recently proposed that the hydrargillite should thermally be decomposed to the α-alumina through dual routes simultaneously, one proceeding directly through a sequence of virtually anhydrous aluminas, namely χ-and κ-modifications, and the other through boehmite followed by a series of other virtually anhydrous aluminas, namely γ-, δ-, and θ-modifications. Both of these two routes lead eventually to a common product, the α-alumina. There remains much to be proved, as to whether or not the formation of the boehmite is of primary nature[7,8,9,10] in this case, and further precise investigations seem necessary in this connection.

It has been confirmed, from an X-ray powder diffraction analysis[5], that the sample 3 of samarium-bearing alumina is almost completely composed of κ-modification. This κ-modification is assumed to be an intermediate alumina produced in one route of the dual thermal transformation from the hydrargillite to the α-alumina. Provided that the X-ray diffraction line in the immediate vicinity of 2.0 Å is caused by the reflection from (400) planes of a spinel lattice[11], its estimated relative intensity would allow us to elucidate whether most of the aluminium ions take their seats in tetrahedral or octahedral interstices of the oxygen network of cubic close-packing. It may probably be concluded, for structural reasons quite similar to those previously made concerning the three prototypes for cathodo-luminescence spectra of praseodymium-bearing aluminas[5] that aluminium ions would fill tetrahedral in preference to octahedral interstices in the decomposition sequence leading directly through anhydrous aluminas. This is likely to be the reason why the luminescence spectrum of the prototype III appears in its genuine form only in the case of samarium-bearing alumina derived from the hydrargillite by a suitable previous heat treatment.

Almost all the luminescence spectra caused by samarium ions existing in numerous samples of anhydrous alumina, which have been obtained in various ways of preparation, may be interpreted as belonging to either one of the three prototypes mentioned above or their combinations.

Conclusion

Cathodo-luminescence spectra given by samarium ions, which have been imbedded in various samples of anhydrous alumina can, according to circumstances, be regarded as belonging to either one of the three luminescence prototypes, namely I, II and III, or their combinations.

It is concluded that the three ways of the reciprocal arrangements for oxygen and aluminium in the configuration of a ground-material, namely alumina in the present cases, may be closely related to the occurrence of these three fundamental spectral types for the samarium-activated luminescence.

The luminescence prototype II mentioned above is obtained with an alumina having the oxygen network of hexagonal close-packing, namely α-modification of alumina, while the luminescence prototypes I and III are caused by aluminas possessing the oxygen network of cubic close-packing.

Which of the last two prototypes of lumi-

7) J.F. Brown, D. Clark and W.W. Elliott, *J. Chem. Soc.*, **1953**, 84.
8) M.K. Day and V.J. Hill, *Nature*, **170**, 539 (1952); *J. Phys. Chem.*, **57**, 946 (1953).
9) T. Sato, *J. Chem. Soc. Japan, Ind. Chem. Section*, **55**, 66 (1952).
10) H.T. Tran et M. Prettre, *Compt. rend.*, **234**, 1366 (1952).
11) G. Ervin, *Acta Cryst.*, **5**, 106 (1952).

nescence is produced, depends probably upon the manner of aluminium ions in occupying the two sorts of interstices of the cubic close-packed oxygen network, namely octahedral and tetrahedral interstices. The luminescence prototype I is seen with γ-modification of alumina, in which aluminium ions are statistically distributed evenly throughout the two sorts of interstices mentioned above, whilst the luminescence prototype III is observed with κ-modification of alumina, where aluminium ions take, for the most part, their seats in the tetrahedral rather than in the octahedral interstices.

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The Scientific Research Institute, Ltd
Komagome, Bunkyo-ku, Tokyo

Cathodo-luminescence of Samarium as Applied to the Structural Studies of Alumina. II. On the Alumina Produced from Hydrous Alumina Gels

By Eiichi IWASE and Seijiro NISHIYAMA

(Received April 25, 1955)

Introduction

Investigations of X-ray powder diffraction patterns showed that hydrous alumina gels freshly produced by a rapid precipitation from cold solutions of aluminium salts are amorphous[1,2]. The hydrous alumina gels are, on calcination, converted to γ-alumina in a wide sense[3,4] through poorly crystallised boehmite, and with progressively increased temperatures, a gradual ordering of cubic close-packed oxygen network takes place, aluminium ions entering into the network by thermal diffusion preferably much more into octahedral than tetrahedral interstices. A low-temperature form of the γ-alumina may be regarded as a modification possessing imperfect and disordered lattices. A complete ordering of aluminium ions is achieved in the cubic close-packed oxygen network by a heat treatment at just below the temperature required for producing α-alumina. This state was called θ-alumina by Stumpf et al.[5] and is considered to be a well-crystallised form of the γ-alumina[6]. The arrangement of oxygen ions varies, on further heating at much elevated temperatures, from cubic to hexagonal close-packing, resulting in the α-alumina or corundum modification of alumina. In this paper an account is given on the mode of changes in a cathodo-luminescence spectrum of samarium ions brought about by heat treatments of samarium-bearing aluminas which have been derived from various alumina hydrogels, and effects of the heat treatments upon the so-called γ-α transformation of alumina are explained.

1) R. Fricke, *Kolloid-Z.*, **69**, 314 (1934).
2) Gmelins Handbuch anorg. Chem., **35**, Aluminium Teil B, 8 Aufl., Verlag Chemie, Berlin, 1934, S. 103.
3) G. Ervin, *Acta Crystal.*, **5**, 103 (1952).
4) Gmelins Handbuch anorg. Chem., **35**, Aluminium Teil B, 8 Aufl., Verlag Chemie, Berlin, 1934, S. 114.
5) H.C. Stumpf, A.S. Russell, J.W. Newsome, and C.M. Tucker, *Ind. Eng. Chem.*, **42**, 140 (1950).
6) G. Ervin, *Acta Crystal.*, **6**, 107 (1952).

Experimental Procedure and Results

Hydrous alumina gels were precipitated by means of neutralisation with ammonia from the solution of one of the following aluminium salts, namely nitrate, sulphate and chloride. These precipitates were washed with water several times on filters, and dried at about 110°C. One gram of each sample of the hydrous alumina gels thus obtained was soaked with 1 ml. of a samarium nitrate solution (the concentration of samarium in this solution is 1% calculated as samarium oxide), dried on a water bath, and ignited at a certain elevated temperature. The resulting samples of samarium-bearing alumina were subjected to cathode-ray bombardment, and cathodo-luminescence spectrograms were taken with a small glass-prism spectrograph of Feuss. The alumina obtained by the ignition at about 930°C for thirty minutes showed, when the aluminium nitrate was employed for the preparation of hydrous alumina gel, broad diffuse luminescence bands belonging to the luminescence prototype I[7], while that at 1000°C for one hour comparatively sharp line-like bands characteristic of the luminescence prototype II[7] (Photo. 1, a). The luminescence spectrum of the prototype I was, however, seen persistently in

7) E. Iwase, This Bulletin, **28**, 596 (1955).

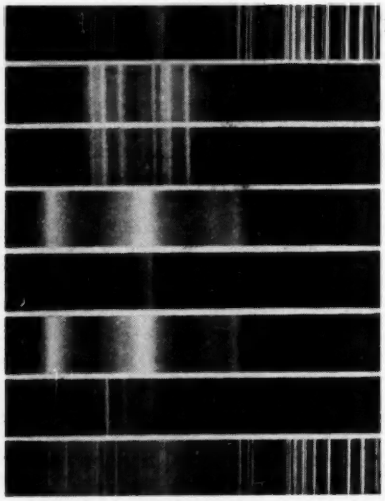

Photo. 1. Reproduction of the cathodo-luminescence spectra of samarium-bearing aluminas derived from various precipitated alumina hydrogels.

Alumina hydrogels were prepared by adding ammonia to solutions of aluminium nitrate (a), (b), of aluminium chloride (c), (d) and of aluminium sulphate (e), (f) respectively. The hydrogels were, after being soaked with a solution of samarium nitrate, converted to alumina by calcination at 1000°C (a), (c), (e) and by roasting in a direct flame of coal gas mixed with oxygen.

the case of alumina derived from either aluminium chloride or aluminium sulphate, without accompanying any band of the prototype II, even though heat treatment had been done at 1000°C for one hour or 1100°C for fifteen minutes (Photo. 1, c and e).

Extremely remarkable differences were observed in cathodo-luminescence spectra of samples of alumina derived from the various alumina hydrogels mentioned above, after being roasted intensely in a direct flame of coal gas mixed with oxygen. The alumina produced by neutralisation of aluminium nitrate solution showed, needless to say, the luminescence spectrum of the pure prototype II (Photo. 1, b), since this had already been attained by calcination at 1000°C, a much lower temperature than that of the present calcination. The alumina derived from the solution of aluminium chloride exhibited, however, a mixed luminescence spectrum of the prototypes I and III (Photo. 1, d), and that from the solution of aluminium sulphate a mixed luminescence spectrum of the prototypes II and III (Photo. 1, f).

It is worthy of note that the most intense luminescence band of the prototype III situated at 596.5~598.0 mμ was seen in the cases of alumina, which had been prepared by precipitation from the solution of aluminium chloride and that of sulphate, and by subsequent ignition in a direct flame of coal gas mixed with oxygen. This luminescence band commenced to appear, after heat treatment had been made at 1200°C for fifteen minutes in the case of alumina derived from the solution of aluminium sulphate. The intensity of cathodo-luminescence bands belonging to the prototype I was decreased in the case of alumina produced from the solution of aluminium chloride, when roasting had been repeated in a direct flame of coal gas mixed with oxygen.

There were observed two luminescence bands at 648~650 mμ and 642~644.5 mμ in a spectral region between 640 and 650 mμ. It is to be mentioned that the former band was more intense than the latter in the case of alumina derived from the nitrate solution, while the order of intensity was reversed in the case of alumina derived from the solution of chloride or sulphate.

Samarium was directly added to dried alumina hydrogels in the experiments so far described. Investigations of cathodo-luminescence spectra of samarium are now being carried out on samarium-bearing samples of alumina, which have been prepared by an addition of samarium at various intermediate stages of thermal decomposition from the hydrous to the anhydrous alumina.

The hydrous alumina gel produced by precipitation with ammonia, was submitted to a previous heat treatment at a certain temperature between 200 and 1000°C. The thermally decomposed samples thus obtained have been soaked with the solution of samarium nitrate and then ignited for one hour over a blast flame of coal gas mixed with air. The samarium-bearing samples of alu-

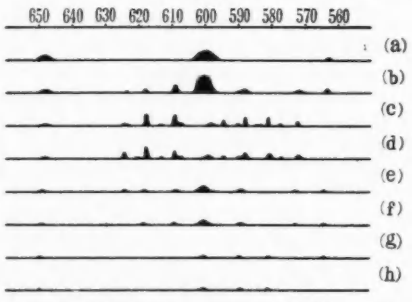

Fig. 1. Schematic representation of cathodo-luminescence spectrum of samarium-bearing alumina derived from the precipitated hydrogel.

Hydrous alumina gels were prepared from a solution of aluminium nitrate by precipitation with ammonia. Prior to the addition of samarium, the alumina gels were dried at 110°C (a), heated for 1 hr. at 200°C (b), at 230°C (c), at 270°C (d), at 300°C(e), at 400°C (f), at 700°C (g), and for 15 min. at 1000°C (h) respectively. All these were finally ignited in a blast flame of coal gas mixed with air.

mina derived from the solution of aluminium chloride or sulphate give always a cathodo-luminescence spectrum belonging to the prototype I, whereas this is not the case with those obtained from the solution of aluminium nitrate. A noteworthy phenomenon has been witnessed with the latter samples. Hydrous alumina gels yielded from the solution of aluminium nitrate, have been washed simply on filters as usual, heated at a temperature either below 200°C or above 400°C, soaked with the solution of samarium nitrate, and then ignited over a blast flame of coal gas mixed with air. These samples of alumina show samarium-luminescence spectra of the prototype I, as can be seen in Fig. 1, (a), (g) and (h).

When previous heat treatment was made at a moderately elevated temperature, namely between 230 and 270°C, and the other experimental conditions mentioned above were maintained, the resulting samples of samarium-bearing alumina give cathodo-luminescence spectra of the plain prototype II (Fig. 1, c and d), although the temperature of final heat treatment was considerably lower than that normally required for the γ-α transformation of alumina.

Experiments quite similar to those described above reveal, with thoroughly purified samples of hydrous alumina gels, that such a striking phenomenon is not encountered, the luminescence spectra being of the prototype I, so far as final ignition has been made over a blast flame of coal gas mixed with air.

Finally, results of investigations are described on hydrous alumina gels produced by immersing for a sufficiently long time crystals of aluminium nitrate enneahydrate, aluminium sulphate octodecahydrate, aluminium chloride hexahydrate and ammonium alum in concentrated solutions of ammonia respectively. The hydrous alumina gels resulting from these reactions were removed from the liquors, washed with water, dried at 110°C, soaked with the solution of samarium nitrate, and then ignited.

Cathodo-luminescence spectra of the prototype I were always obtained with samarium-bearing samples subjected to a moderate ignition over a blast flame of coal gas-air. These samarium-bearing samples showed, after ignited intensely in a direct flame of coal gas mixed with oxygen, cathodo-luminescence spectra of the prototype II, but a luminescence spectrum of the prototype III[7] appeared overlapping that of the prototype II in the cases of samarium-bearing alumina derived from hydrated crystals of aluminium chloride and aluminium sulphate.

Discussion

According to Biltz's X-ray investigations[8], hydrous alumina gels yielded through neutralisation of a solution of aluminium sulphate with ammonia gave γ-modification of alumina, when subjected to heat treatments between 150 and 500°C. Hansen[9] also stated that hydrous alumina gels derived from a solution of aluminium chloride by precipitation with ammonia, was converted to the γ-alumina, when calcined at temperatures between 600 and 1000°C. A thermal transformation was said to proceed gradually from γ- to α-alumina, and various temperatures were given for this transformation namely 950°C or higher[10], 1000°C[11], above 1000°C[12] and 1000~1200°C[13].

From the present authors' investigations on the feature of the cathodo-luminescence spectrum it is found that alumina gels derived from solutions of various aluminium salts show some differences in the temperature for the γ-α transformation, when samarium was added to the dried original hydrogels and the thermal transformation was caused in the presence of the samarium; the alumina hydrogel derived from a solution of aluminium nitrate is transformed into the α-modification at temperatures between 930 and 1100°C, while that from a solution of aluminium chloride or sulphate is so far unable to be transformed by an intense heat treatment at 1100°C. Weiser[14] stated that a remarkable difference in the size of the constituting particles was confirmed by X-ray studies between the hydrous alumina gels produced from aluminium nitrate and those from either aluminium sulphate or chloride. This statement seems to deserve to be referred to in connection with the above-mentioned observations. There are also marked distinctions in the cathodo-luminescence spectrum between the alumina derived from a solution of aluminium chloride and that from a solution of aluminium sulphate, both samples of alumina being roasted at more elevated temperatures.

A peculiar configuration, namely the κ-modification of alumina, begins to be formed in some parts of the alumina derived from a solution of aluminium sulphate by heat treatment at 1200°C for fifteen minutes, the configuration being responsible for giving rise to the most intense luminescence band of the prototype III. This particular configuration is locally produced in corundum structure, when a much stronger heat treatment is made in a direct flame of coal gas

8) W. Biltz, A. Lemke und K. Meisel, *Z. anorg. Chem.*, **186**, 373 (1930).

9) W.C. Hansen and L.T. Brownmiller, *Am. J. Sci. Sill.*, (5), **15**. 225 (1928).

10) E.J.W. Verwey, *Z. Krist.*, **91**, 65 (1935).

11) W. Biltz, A. Lemke und K. Meisel, *Z. anorg. Chem.*, **186**, 377 (1930).

12) G. Hägg und G. Söderholm, *Z. physik. Chem.*, B **29**, 93 (1935).

13) A.N. Winchell, "The Microscopic Characters of Artificial Inorganic Solid Substances or Artificial Minerals", John Willy & Sons, Inc., New York, p. 189 (1931).

14) H.B. Weiser and W.O. Milligan, "Advance in Colloid Sciences", **1**, 227 (1942)

mixed with oxygen. Thus the alumina obtained here does not consist of the simple corundum. The resulting alumina is composed of the mixture of γ- and κ-modifications, when the hydrogel derived from a solution of aluminium chloride has been subjected to an intense roasting in a direct flame of coal gas mixed with oxygen. The amount of its γ-ingredient is decreased by repeated heat treatments.

It was already presumed by one of the present authors[7] that the luminescence bands of the prototype III are perceptible, when the samarium ions exist in such an alumina that its constituting aluminium ions are situated favourably in tetrahedral rather than in octahedral interstices of cubic close-packed oxygen network. Verwey[15] compared the X-ray diagram of an ordinary spinel with that of the γ-alumina prepared by careful heating of aluminium hydroxide, which had been precipitated with ammonia, and thus arrived at a conclusion that octahedral interstices of the oxygen network are not filled up by aluminium ions in this γ-alumina. Hence, his conclusion is concordant with the postulation presented by one of the present authors, which has been deduced from investigations of the cathodo-luminescence spectra of samarium ions.

In short, the studies on the cathodo-luminescence spectra of samarium indicate that samples of alumina produced by neutralisation of solutions of aluminium nitrate, sulphate and chloride with ammonia, have constructions different from one another. This fact might naturally be related to the complicated characters shown by various kinds of alumina hydrogel, when they are employed as catalysts in some chemical reactions.

An impregnation of samarium ions may possibly stabilise the transient stage caused by thermal decomposition of hydrous alumina gels, and these stages would, in some cases, remain fixed in samples of anhydrous alumina obtained by the subsequent calcination at just below the temperature necessary for production of the α-modification, since the large samarium ions might pack structural defects yielded during the course of thermal destruction of the hydrous alumina gels. This expectation is usually not fulfilled in the cases of hydrous alumina gels produced by precipitation with ammonia, irrespective of the different kinds of aluminium salts employed for the preparation of these alumina gels, the γ-modification of alumina being always obtained, which is confirmed by the feature of the cathodo-luminescence spectrum of the impregnated samarium. However, the intermediate configurations caused by suitable thermal treatments are, in the case of hydrous alumina gels derived from a solution of aluminium nitrate, likely made fixed by the impregnated samarium ions. The hydrous alumina gel in question was previously heated at a medium temperature, namely between 230 and 270°C for one hour, and the impregnation of samarium ions was made for the purpose of stabilising the intermediate configuration thus yielded. The samarium-bearing alumina resulting from a subsequent ignition in a blast flame of coal gas-air, gives a cathodo-luminescence spectrum of the plain prototype II, although the temperature of final heat treatment has been considerably lower than that normally required for the γ-α transformation of alumina. An X-ray diffraction investigation has also shown that this sample of alumina consists of the α-modification. It should accordingly be presumed that the configuration yielded intermediately through the special heat treatment, closely resembles the structure of the α-modification of alumina, which is fixed by the packing of the impregnated samarium ions.

The content of water and that of ammonium nitrate, the latter being the by-product of the neutralisation reaction, are estimated for the original sample of this hydrous alumina gel to be 1.00 and 0.39 g. of the resulting alumina respectively, while the water content is, in the samples partially decomposed by the special previous heat treatments at 230 and 270°C, reduced to 0.31 and 0.26 g. respectively and the ammonium nitrate content is also reduced to 0.30 and 0.06 g. respectively. The hydrous alumina gels mentioned above were produced by a simple washing on filters and not entirely free from the reaction by-products. In the case of hydrous alumina gel produced by neutralisation with ammonia, of a solution of aluminium nitrate, the reaction by-product, namely the ammonium nitrate remaining in the gel, seems to act, when its amount is moderate, as something like a mineraliser for accelerating the transformation into the α-modification on being heated at much lower temperatures. A series of experiments indicates that such a striking effect is scarcely ever observed with the carefully purified samples of hydrous alumina gels.

The purified samples derived from a solution of aluminium nitrate were, after ammonium nitrate had been added to each of them in varying amounts, subjected to a mild heat treatment at 250°C for one hour, soaked

15) E.J.W. Verwey, *Z. Krist.*, **91**, 69 (1935).

with the solution of samarium nitrate, and then calcined over the flame of coal gas mixed with air. All the resulting samples of samarium-bearing alumina show nothing but the cathodo-luminescence spectrum of the prototype I. Thus it becomes apparent that no extraordinary effect is produced, once the ammonium nitrate intimately held in the original alumina hydrogel has been removed, and a subsequent addition of ammonium nitrate can no more act as a special mineraliser for yielding the α-modification of alumina.

Summary

Hydrous alumina gels were prepared from both solutions and crystals of a number of aluminium salts, in the former case by precipitation with ammonia and in the latter by direct immersion in concentrated ammonia liquor. Samarium ions were impregnated in these hydrous alumina gels or in their transition phases resulting from the previous thermal treatment of various temperatures. The feature of the cathodo-luminescence spectrum was investigated on the samarium-bearing alumina produced from the above-mentioned samples by a final heat treatment.

Spectrographic measurements of the cathodo-luminescence reveal that the heating of the hydrous alumina gels derived from a solution of aluminium nitrate results in their conversion to the α-alumina, while the heating of those from solutions of aluminium chloride and sulphate does not give the genuine α-modification. This was confirmed by the fact that the most intense band of a particular luminescence prototype III as designated by one of the present authors was observed in the cathodo-luminescence spectra.

The γ-α transformation of alumina occurs at temperatures far below its transition temperature when a suitable amount of ammonium nitrate, the by-product of the neutralisation reaction, was caused to remain by heating the precipitated hydrous alumina gel, which was derived from a solution of aluminium nitrate at a moderately elevated temperature.

Similar remarkable results were, however, not obtained with hydrous alumina gels derived from solutions of aluminium chloride and sulphate, and also with the gel derived from a solution of aluminium nitrate, if the latter gel had been made free from the reaction by-product. An addition of ammonium nitrate to the purified alumina gels can no more regenerate the ability to accelerate the γ-α transformation.

It is interesting to note that hydrous alumina gels obtained by immersing crystals of aluminium nitrate enneahydrate, aluminium chloride hexahydrate, aluminium sulphate octodecahydrate and ammonium alum in concentrated ammonia liquor for a sufficiently long time behave themselves, on being heated, in a somewhat similar way to those obtained by precipitation from the solutions of the foregoing aluminium salts.

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The Scientific Research Institute, Ltd., Komagome, Bunkyo-ku, Tokyo

*The Structon Theory of Glasses and Solutions**

By Maurice L. HUGGINS**

(Received August 29, 1955)

Introduction

Many properties of liquids and solids can usefully be considered as dependent on the kinds and numbers of "structon" present. This word, "structon," has been invented by the writer[1,2]. It may be defined as "an atom (or molecule or group of atoms of a given kind) in a given environment." The structon concept is especially valuable when considering properties which are approximately additive—that is, which can be made up of contributions of the different types of structon present. Volume and molar refraction are examples of such properties. Certain thermodynamic functions, such as energy and heat content, would also be expected to be approximately structon-additive. As would be expected, structon additivity is usually somewhat better than atomic or molecular additivity.

The "environment" referred to here is that of closest neighbors only. More distant atoms or molecules are considered to be of negligible influence on the properties dealt with.

This paper deals primarily with solutions—both solid solutions (such as ordinary glasses) and liquid solutions. The usefulness of the structon concept is most evident in dealing with solutions in which different structon types differ so much in stability that, over a composition range, only those few types exist, in significant relative amounts, which are the most stable.

Glasses

Well-annealed sodium silicate glasses conform to this requirement, as will be shown. These glasses have a structural arrangement which was stable at a high temperature and which has been frozen in as the glass cooled. A graph of the volume as a function of the composition (Fig. 1[3-6]) shows straight-line segments, with sharp breaks between them. It has generally been assumed that behavior of this sort indicates compound formation, but x-ray studies[7] give no evidence of compounds.

The writer has proposed[1,2] the alternative explanation that in each composition range there are only a few types of structons, the breaks occurring at compositions at which one type of structon disappears and another appears.

Consider first the structure of pure silica, SiO_2. Many years ago the writer[8] showed that in crystalline silica (quartz) each silicon atom is surrounded by four close oxygen neighbors and each oxygen atom is adjacent to two silicons. The structure may be described as being composed of structons of the two types represented by the formulas Si(4.0) and O(2Si).

It does not matter, for present purposes, whether one considers the forces between adjacent silicon and oxygen atoms to be essentially covalent or ionic. Actually, there is good reason to believe that they are intermediate in character, involving electronpair bonds with a considerable degree of polarity.

In *vitreous* silica, x-ray and other evidence shows that the same two structon types exist, practically exclusively, as in crystalline silica.

If a little sodium oxide is added to silica and a glass is produced, there must of course be some new types of structons. The types to be considered may be limited to a few, either on the basis of simple theoretical considerations or, reasoning by analogy, making use of the large body of information which has been accumulated regarding the structures of *crystalline* silicates. All of the sodium atoms (or ions) would be expected to be surrounded by oxygens, with no sodium-silicon contacts. The number of oxygens around each sodium, for greatest stability, cannot be assumed *a priori*, but a good guess would be six. There would then be structons

* Communication No. 1746 from the Research Laboratories of the Eastman Kodak Company, Rochester 4, New York, U.S.A.

** Fulbright Exchange Professor, Osaka University, and Lecturer, Kyoto University, 1955-56.

1) M.L. Huggins, *J. Phys. Chem.*, **58**, 1141 (1954).

2) M. L. Huggins, *J. Am. Ceramic Soc.*, **38**, 172 (1955).

3) M.L. Huggins and K.H. Sun, *Glass Industry*, **24**, 472 (1943).

4) F.W. Glaze, J.C. Young and A.N. Finn, *Bur. Stand. J. Res.*, **9**, 799 (1932).

5) G.W. Morey and H.E. Merwin, *J. Opt. Soc. Am.*, **22**, 632 (1932).

6) S.R. Scholes, "Handbook of the Glass Industry", Ogden-Watney Publishers, Inc., New York, N.Y. (1941), p. 61.

7) See, for example, B.E. Warren, *J. Appl. Phys.*, **8**, 645 (1937), or *J. Am. Ceramic Soc.*, **24**, 256 (1941).

8) M.L. Huggins, *Phys. Rev.*, **19**, 363 (1922).

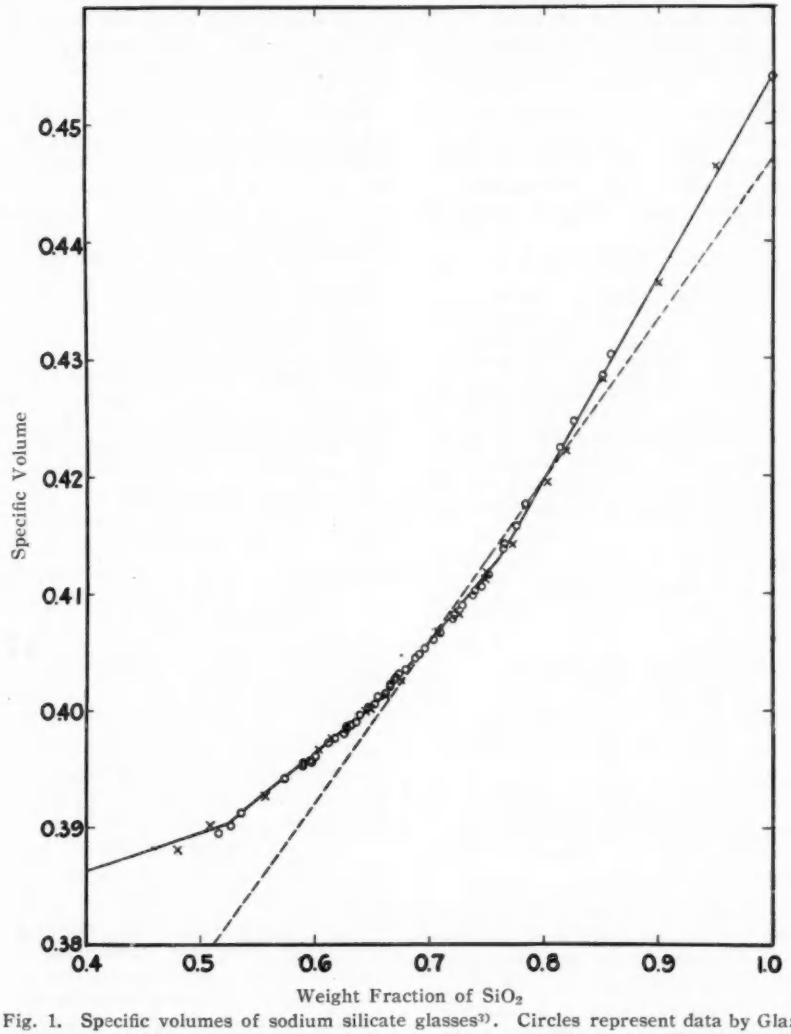


Fig. 1. Specific volumes of sodium silicate glasses[3]. Circles represent data by Glaze, Young, and Finn[4]; crosses denote data by Morey and Merwin[5]. The dashed line represents a relationship given by Scholes[3].

of formula Na(6.0). One would expect some oxygens to be surrounded by two silicons (as in pure silica), plus one sodium. An environment of two silicons and *two* sodiums would require a greater departure from short-range neutrality, and so would be less reasonable. As a rough measure of this departure, one can calculate a hypothetical "structon charge," by considering the structure as composed of sodium, silicon, and oxide *ions* and adding algebraically the charge on an oxygen (–2) and the appropriate shares of the charges on each of the ions surrounding that oxygen: +4/4 for each silicon neighbor and +1/(coordination number of the sodium) for each sodium neighbor.

There must also be oxygen-centered structons in which the central oxygen has less than two silicon neighbors. Oxygen-centered structons with only sodium neighbors (essentially oxide ions) have never been found in silicate crystals and would be unreasonable theoretically. Oxygen-centered structons with only one silicon neighbor would be expected to have some sodium neighbors, enough to give a close approach to regional

neutrality. The number is *a priori* unknown.

The minimum number of structon types capable of giving the over-all composition is five (See the section on "The Structon Number Rule"). For any given set of five types which one chooses to assume, it is easy to compute the limits of existence of the set and, within those limits, the relative numbers of structons of each type. The procedure may be illustrated for the following assumed set:

Si(4.0) Na(6.0) O(2Si) O(2Si, Na) O(Si, 3Na).

For convenience, an amount of glass which contains, on the average, one oxygen atom is considered. The number of structons of each type in this amount of glass is designated as N, with the appropriate structon formula as subscript. The numbers of silicon and sodium atoms in this amount of glass are represented as N_{Si} and N_{Na}, respectively.

With these definitions, the sum of the numbers of oxygen-centered structons equals unity:

$$N_{O(2Si)}+N_{O(2Si,\ Na)}+N_{O(Si,\ 3Na)}=1 \qquad (2)$$

The number of oxygen-to-silicon contacts equals the number of silicon-to-oxygen contacts. Hence,

$$2N_{O(2Si)}+2N_{O(2Si,\ Na)}+N_{O(Si,\ 3Na)} = 4N_{Si(4.0)}=4N_{Si} \qquad (2)$$

Likewise, the number of oxygen-to-sodium contact equals the number of sodium-to-oxygen contacts:

$$N_{O(2Si,\ Na)}+3N_{O(Si,\ 3Na)}=6N_{Na(6.0)}=6N_{Na} \qquad (3)$$

The valences must be balanced, to satisfy the requirement that the glass as a whole be electrically neutral. Hence,

$$4N_{Si}+N_{Na}=2 \qquad (4)$$

By solving the foregoing equations simultaneously, the numbers of the different types of structon are obtained as functions of the composition. If the composition is expressed as N_{Si}, the equations are as follows:

$$N_{Si(4.0)}=N_{Si} \qquad (5)$$

$$N_{Na(6.0)}=2-4N_{Si} \qquad (6)$$

$$N_{O(2Si)}=-7+16N_{Si} \qquad (7)$$

$$N_{O(2Si,\ Na)}=6-12N_{Si} \qquad (8)$$

$$N_{O(Si,\ 3Na)}=2-4N_{Si} \qquad (9)$$

The limits of the composition range, within which this assumed set of structons is capable of existence, are the compositions at which the numbers of one or more of the structon types become zero. The maximum value of N_{Si} is 1/2, the value in pure silica. Then, according to Eqs. 6, 8, and 9, the number of structons of each of the types, Na(6.0), O(2Si, Na) and O(Si, 3Na), becomes equal to zero. The minimum value of N_{Si} is 7/16, the composition at which the O(2Si) structons disappear. ***This is at precisely the location of the first break in the curve representing the experimental volume data*** (See Fig. 2[9,10,11]).

Similar calculations have been made for all other sets of structons which seem at all reasonable. All sets give a lower limit for N_{Si} which is in disagreement with experiment, except those which are like the set just considered, except for replacement of Na(6.0) and O(Si, 3Na) by Na [$(w+3)$O] and O(Si, wNa), with w equal to an integer. The choice of $w=3$, giving the structons tentatively assumed, seems to be the most reasonable. Moreover, other choices lead to disagreement with experiment in the next composition range. It seems necessary to conclude that the chosen set of structons is the one actually existing in these glasses in this composition range.

A similar analysis leads to the conclusion that in Range II, with N_{Si} between 0.40 and 0.4375, the only structons present in significant amounts are the following:

Si(4.0) Na(6.0) O(2Si, Na)
O(2Si,2Na) O(Si, 3Na)

For N_{Si} less than 0.40, there are several possibilities, between which the data now being considered do not enable one to distinguish. A reasonable set for the range $0.375<N_{Si}<0.40$ would be the following:

Si(4.0) Na(6.0) Na(5.0) O(2Si, 2Na) O(Si, 3Na)

This might be followed, for $0.333<N_{Si}<0.375$, by the set:

Si(4.0) Na(5.0) O(2Si, 2Na)
O(Si, 3Na) O(Si, 4Na)

At the sodium metasilicate composition, $N_{Si}=0.333$, the O(Si, 3Na) structons would necessarily disappear. The four remaining types are those occurring in the crystalline compound of this composition[12].

From these assumptions, or any of several others which also appear reasonable, one would expect a break in the property-composition curve at $N_{Si}=0.375$. The contributions of the different structon types might be such, however, as to make the break a very minor one. Experimentally (Fig. 2), the volume data are insufficient to tell whether or not a small break actually occurs at this composition.

From the slopes and intercepts of the straight-line segments of the experimental

9) F. Winks and W.E.S. Turner, *J. Soc. Glass Technol.*, 15, 185T (1931).
10) M.L. Huggins, *J. Opt. Soc. Am.*, 30, 420 (1940).
11) M.L. Huggins, *Ind. Eng. Chem.*, 32, 1433 (1940).
12) P.A. Grund and M.M. Pizy, *Acta Cryst.*, 5, 837 (1952).

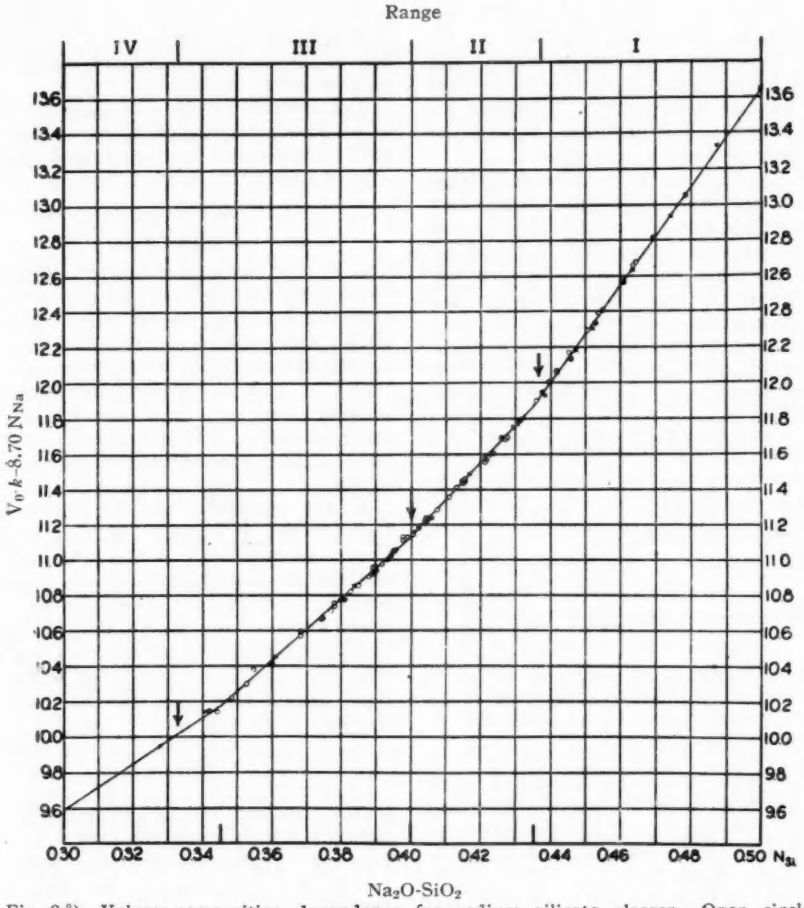


Fig. 2.[2] Volume-composition dependence for sodium silicate glasses. Open circles represent data of Glaze, Young, and Finn[4]; crosses denote data by Morey and Merwin[8]. Solid circles denote data by Winks and Turner[9] The small constant, k, is included to allow for difference in annealing techniques. The straight lines conform to relationships deduced empirically,[10,11] which differ very slightly from those recently obtained theoretically[1,2].

volume-composition curves, it is possible to deduce some relationships between the volume contributions of the different structon types. Their individual contributions, however, cannot be deduced from the data for this system alone. When suitable measurements are made for other systems containing some of the same types of structons, it should be possible to compute the individual structon contributions to the total volume. Similar remarks apply with respect to other additive properties.

Liquid Solutions

The structon types existing in most liquid solutions include not only those in the set giving the lowest free energy, but also others, only slightly less stable, in dynamic equilibrium with them. It is possible, using well-known methods, to develop a quantitative theory of such solutions, relating the numbers of the different types of structons to their relative energies and to the over-all composition. These numbers can then be used as a basis for the theoretical calculation of various additive properties.

The present discussion, however, will be limited to consideration of a few molecular solutions which can be dealt with in much the same manner as the sodium silicate glasses. The essential requirement for this is that there are strong intermolecular inter-

actions of only one type or of only a few types, differing sufficiently in stability from one another. Many solutions in which their is strong intermolecular hydrogen-bonding conform to this requirement. Evidence for this is the observed broken-line dependence of certain properties on composition.

In these solutions it is the *molecular*, rather than the *atomic*, environment which is important for the present purpose, hence "molecular-structon" types will be discussed. Since the hydrogen-bond forces between molecules are much stronger than those of other types, only hydrogen-bonded neighbors need be specified in characterizing the structons.

As a first example, consider dilute solutions of dimethyl formamide and phenol in carbon tetrachloride. As is shown by Fig. 3[13], taken from a recent paper by Arshid et al.,[13] a

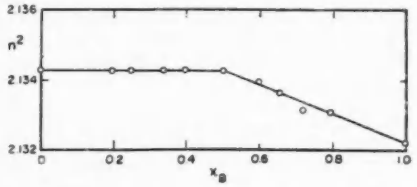


Fig. 3.[13] Variation of refractive index (n) with composition, for solutions of dimethyl formamide (A) and phenol (B) in carbon tetrachloride.

plot of the square of the refractive index against the relative proportions of dimethyl formamide and phenol shows two portions which are essentially straight, meeting at the equimolar composition.

This behavior is consistent with the assumption that the forces between like molecules are much weaker than those between unlike molecules, and that the latter produce a 1 : 1 complex, presumably by hydrogen-bonding:

$$\begin{matrix} R_2N-CH=O\cdots\cdots HO-C_6H_5 \\ A\cdots\cdots\cdots\cdots B \end{matrix}$$

The sets of structons can be represented as follows:

Range I:	A(O)	A(B)	B(A)	
Range II:		A(B)	B(A)	B(O)

Here, A(O) designates an A molecule which has no strong interaction with any of its neighbors, A(B) denotes an A molecule strongly attached to a single B neighbor, etc. (Note that "O" in these molecular-structon formulas represents "zero," not "oxygen").

The experimental curves might also be interpreted in terms of a complex of formula A_2B_2 or A_3B_3 or A_iB_i, with i any integer, but in this case the simplest formula seems as reasonable as any.

The relative numbers of the different types of structons (in Range I, for example) are readily computed from the following relationships between the mole fractions:

$$x_{A(O)}+x_{A(B)}+x_{B(A)}=1 \qquad (10)$$

$$x_{A(B)}=x_{B(A)} \qquad (11)$$

The first of these is a normalizing equation, expressing the requirement that the sum of the mole fractions equals unity. The second shows that the sum of the A-B contacts equals the sum of the B-A contacts. The limits of this range, at mole fractions of phenol equal to zero and 1/2, are the concentrations at which, according to these equations, the mole fraction of at least one of the structon types equals zero.

In the equimolar solution, the only structons present are of the A(B) and B(A) types. From the properties of this solution, one can deduce the contributions of the A·····B complex, but not (without supplementary assumptions) those of the individual structons.

It may be noted that the refractive index squared, which is plotted in Fig. 3, is not itself an additive property, but is related[14,15] by the simple equation

$$n^2=1+\frac{R}{V} \qquad (12)$$

to the (Newton) refraction and the volume, both of which would be expected to be approximately structon-additive. Breaks in the plot of n^2 *versus* composition would be expected, at the same compositions as breaks in the R and V curves, i.e., at the points where changes of structon type occur.

Because of the proportionality between the dielectric constant and the square of the refractive index (for long wavelengths), one would expect dielectric constant *versus* composition curves to exhibit the same sort of

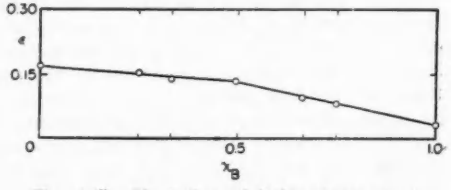


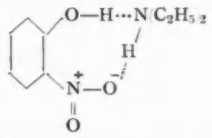
Fig. 4.[16] Variation of dielectric constant (ϵ) with composition, for solutions of *o*-nitrophenol (A) and diethylamine (B) in benzene.

13) F.M. Arshid, C.H. Giles, E.C. McLure, A. Ogilvie and T.J. Rose, *J. Chem. Soc.* (London), 1955, 67.

14) M.L. Huggins, *J. Opt. Soc. Am.*, 30, 495 (1940).

15) M.L. Huggins, *J. Am. Chem. Soc.*, 63, 116 (1941).

peculiarities as the corresponding squared refractive index curves. This is illustrated by Fig. 4[16], representing data for solutions of *o*-nitrophenol and diethylamine in benzene[16]. A 1:1 complex is again indicated. A reasonable structure would be that indicated by the formula.



With new definitions of A and B, the discussion given above for the (dimethylformamide)-phenol system is applicable.

The dielectric constant curve[16] (Fig. 5) for

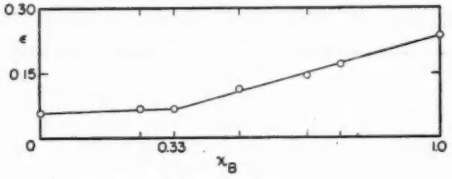


Fig. 5.[16] Variation of dielectric constant with composition, for solutions of azobenzene (A) and aniline (B) in benzene.

benzene solutions of azobenzene (A) and aniline (B) shows a sharp break at the 2:1 composition, indicating the formation of a complex of formula $A_{2i}B_i$, with i indeterminate without further information. The structon sets in the two composition ranges are presumably the following:

Range I: A(O) A(iB) B(2iA)
Range II: A(iB) B(2iA) B(O)

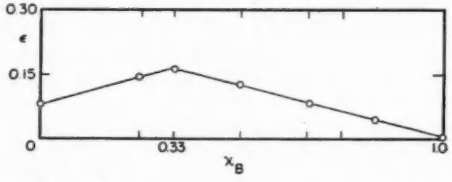


Fig. 6.[16] Variation of dielectric constant with composition, for solutions of phenol (A) and quinol (B) in diethyl ether.

The dielectric constant curve[16] (Fig. 6) for mutual solutions of phenol (A) and quinol (B) in diethyl ether also show a break at $x_B=1/3$. In this case, the most reasonable interpretation is that each phenol molecule is hydrogen-bonded to *two* quinol molecules and each quinol molecule to *four* phenol molecules. To account for the break in the curve, it seems necessary to assume that the hydrogen bonds to the ether molecules are considerably weaker and may be neglected.

An alternative way of looking at this system is to consider the hydroxyl hydrogen atoms (H), the phenol residues (P), and the quinol residues (Q) as the components of the structons, and to assume that every hydroxyl hydrogen is hydrogen-bonded to an oxygen of another hydroxyl. The observed break is then accounted for by the following sets of structon types and hydrogen-bond types:

Range I: P(2H) Q(4H) H(2P) H(P, Q)
H··· bonds: PHP PHQ
Range II: P(2H) Q(4H) H(P, Q) H(2Q)
H··· bonds: PHQ QHQ

The dielectric constant curve[16] for solutions of phenol (A) and azobenzene (B) in water shows two breaks, at $x_B=1/3$ and 1/2 (Fig. 7). This is most simply accounted for

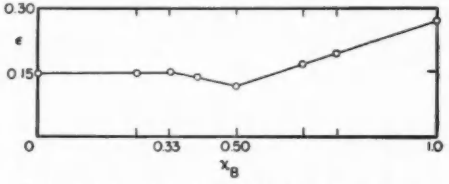


Fig. 7.[16] Variation of dielectric constant with composition, for solutions of phenol (A) and azobenzene (B) in water.

by the following sets of structons and aggregates:

Range I: A(O) A(B) B(2A)
Aggregates: A_2B
Range II: A(B) B(2A) B(A)
Aggregates: A_2B AB
Range III: A(B) B(A) B(O)
Aggregates: AB

An especially interesting system is that of phenyl isothiocyanate (A) and diethylamine (B). The viscosity curve at 25°C, published by Kurnakov and Zemchuzny[17] in 1913, shows a very high, sharp maximum at the equimolar point, suggesting the presence of long-chain polymers (Fig. 8). As the temperature is raised, the height of the peak decreases, presumably because of decreasing average chain length. This indicates that the forces holding the units together in the molecular chain are either hydrogen-bond forces or others of similar magnitude.

The loss factor, ε'', of the microwave dielectric constant likewise shows a peculiar

16) C.H. Giles, T.J. Rose and D.G.M. Vallance, *J. Chem. Soc.* (London), 1952, 3799.

17) N. Kurnakov and S. Zemchuzny, *Z. Physik. Chem.*, 83, 481 (1913).

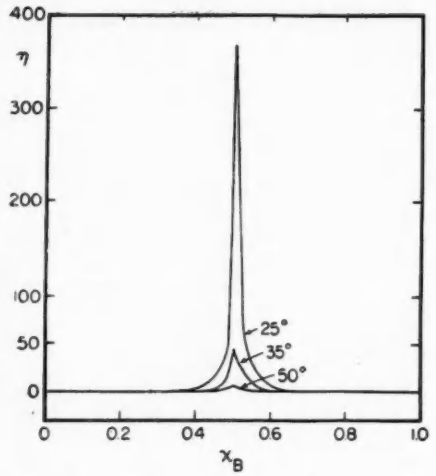


Fig. 8.[17] Variation of viscosity (η) with composition, for binary solutions of phenyl isothiocyanate (A) and diethylamine (B).

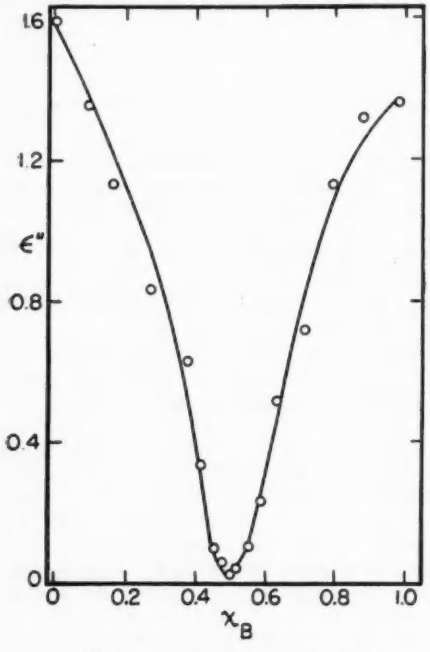


Fig. 9.[18] Variation of microwave dielectric loss (ε'') with composition, for binary solutions of phenyl isothiocyanate (A) and diethylamine (B).

behavior for this system[13]. A low, sharp minimum occurs at the equimolar point (Fig. 9).

18) P.K. Kadaba, *J. Chem. Phys.*, **22**, 1465 (1954).

The following sets of structon and aggregate types are tentatively suggested, pending further experimental work, as reasonable ones to account for this behavior:

Range I: A(O) A(B) B(2A)
Aggregates: A_2B
Range II: A(B) B(2A) A(2B)
Aggregates: $(AB)_t$ $(AB)_tA$
Range III: B(2A) A(2B) B(A)
Aggregates: $(AB)_t$ $B(AB)_t$
Range IV: A(2B) B(A) B(O)
Aggregates: AB_2

On this basis, there are only small aggregates in Ranges I and IV, but Ranges II and III contain chain molecules (and perhaps ring molecules also). Assuming strict adherence to this scheme, but neglecting ring formation, the average molecular weight depends on composition as shown in Fig. 10.

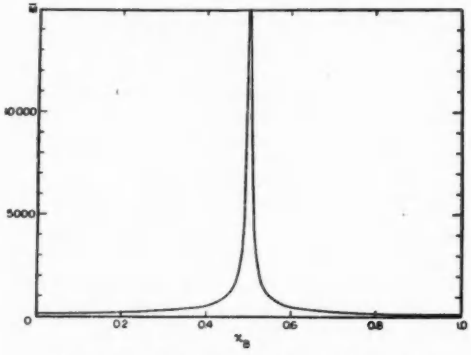


Fig. 10. Variation of calculated average molecular weight ($\bar{M}$) with composition, for binary solutions of phenyl isothiocyanate (A) and diethylamine (B).

The calculated molecular weight curve closely follows that of the 25°C viscosity curve, except that the former goes to infinity at the equimolar composition. This correspondence would be expected theoretically for solutions containing linear polymers[19].

Discussion of the nature of the association between the molecules in these polymer chains will be postponed until later.

In the literature, there are many other examples[13,15,20,21] of property-composition curves, for solution systems, which exhibit sharp breaks. In all cases of which the author is aware, it would be reasonable to assume association, usually involving hydro-

19) M.L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939).
20) V.S. Griffiths, *J. Chem. Soc.* (London), **1952**, 1326.
21) G.N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, N.Y. (1923), p. 40.

gen bonds. Structon theory should be applicable, in most instances at least.

Although, in many cases, the breaks in the experimental curves can equally well be interpreted in terms of the formation of compounds or strong complexes of suitable compositions, the structon concept is more general and is more appropriate in cases in which linear or net work polymeric complexes are formed: for example, in the phenol-quinol, (phenyl isothiocyanate)-diethylamine, and sodium silicate systems. Another advantage of this point of view is that it makes possible the calculation of various properties of structon types, these properties presumably being transferable from system to system.

The Structon Number Rule

The minimum number of structon types in a given system at a given concentration or over a given concentration range is given by a rule which can be called "the structon number rule," by analogy with the phase rule[22].

The minimum number (S) of structon types is equal to the number of equations required to fix the numbers of structons of each type. There is one equation for each of C types of contact between structon centers, representing the fact that there are as many B contacts to A centers as A contacts to B centers. There is a normalizing equation, expressing the requirement that the total amount of matter in the structons equals that in the quantity of matter being considered, or the requirement that the sum of the mole fractions equals unity. In many cases (e.g., in the glasses discussed above, other than pure silica), the relative numbers of structons of different types are also limited by a neutrality or valence-balancing equation. There is an additional equation for each degree of composition freedom (F).

The structon number rule can thus be expressed as

$$S=C+F+2 \qquad (11)$$

if the neutrality limitation is required, and

$$S=C+F+1 \qquad (12)$$

otherwise.

Further Development

This theory can obviously be developed and extended in several ways. For example, the contributions of the individual structon types to specific properties of interest can be deduced and interpreted in terms of structon structure. It should be possible to relate the existence of structon types and of particular sets of them to energies of interaction between the atoms, ions, and molecules concerned. A quantitative treatment of these relationships should enable one to deal with systems showing departures from strict linearity of (structon-additive) property-composition curves, rounding at the breaks between ranges, etc., relating these phenomena quantitatively to the presence of structons other than those of lowest energy.

Another line of future extension of the theory is to polymer systems, in which the chief intermolecular interactions are strong attractions between atomic groups of specific kinds.

Summary

In sodium silicate glasses and in many liquid solutions, curves representing the dependence of various properties on composition show distinct breaks. This behavior can be reasonably interpreted in terms of the types of environment around each atom or molecule or atomic group responsible for strong intermolecular interactions, together with the assumption that in these systems only the most stable environments are present in significant amounts. Only closest neighbors need be considered, hence the types of environment can conveniently be described in terms of "structons," each structon type being defined as a given kind of atom (or molecule or atomic group) surrounded by close neighbors in a given way.

The compositions at the breaks in the property curves limit, and in some cases determine uniquely, the types of structon present in and between the different composition ranges.

The structon theory has been applied to sodium silicate glasses and certain liquid solutions, in which there are strong hydrogen-bond interactions between molecules.

The Research Laboratories of the Eastman Kodak Company, Rochester 4, New York, U. S. A.

22) M. L. Huggins, *J. Am. Chem. Soc.*, **77**, 3928 (1955).

SHORT COMMUNICATIONS

Formation of Formoguanamine by the Reaction between Cyanamid and a Reduced Compound of Free Guanidine (Studies on Some Derivatties of Cyanamide XLV**)*

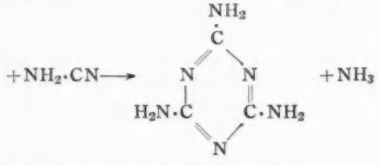
By Keijiro Odo, Kozo Shirai and Kiichiro Sugino

(Received June 27, 1955)

It seemed to us that the reaction between cyanamide and free guanidine in alcoholic solution has hitherto not been studied. So, an investigation was made in order to clarify the products of this reaction.

First, the authors expected biguanide as a primary reaction product and melamine as a final product. But it was found that entirely different products were obtained in accordance with different procedures of the preparation of free guanidine. When a solution of free guanidine in ethanol was prepared by adding an equivalent amount of guanidine salt (for example, guanidine hydrochloride) to a sodium ethylate solution, it reacted with cyanamide to give biguanide just as we expected. But the reaction was found to proceed very slowly, so that only a trace of biguanide was formed even when the mixture was heated at 70–80°C for two hours[1]. And biguanide itself was found to give melamine when it was treated with cyanamide in ethanol. These reactions can be represented as follows.

$$NH_2\cdot C(NH)\cdot NH_2 + NH_2\cdot CN \longrightarrow NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2$$



But when a solution of free guanidine was prepared by adding an equivalent amount of metallic sodium to a solution of guanidine salt in ethanol, it reacted with cyanamide to give formoguanamine in a fair yield. This reaction seemed to be very rapid as compared with the formation of biguanide from guanidine.

For a typical run, 47.77 g. (0.50 mole) of thoroughly dried guanidine hydrochoride was dissolved in 250 cc. of absolute ethanol and 11.50 g. (0.50 mole) of clean sodium cuttings was added piece by piece with agitation, keeping the temperature at 20–30°C. A small quantity of ammonia was evolved during the dissolution of sodium (refer to Fig. 1). In the resulting solution, about 75% of guanidine used was found to remain as free base, but about 25% of it was supposed to be converted to a reduced form which could not be precipitated as picrate. 11.05 g. (0.25 mole) of cyanamide crystal (purity 95% was added to this solution without separating sodium chloride and the mixture was warmed gradually under reflux on the steam bath with slow stirring. When the temperature reached about 40°C, the reaction began to occur with the evolution of ammonia The reaction mixture was continued to heat till the temperature reached 80°C and maintained at that temperature for 30 minutes. (total reaction time: 3 hours and 20 minutes). In Fig. 1, are plotted the quantity of ammonia evolved and the reaction temperature against time which shows the proceeding of the over-all reaction accurately.

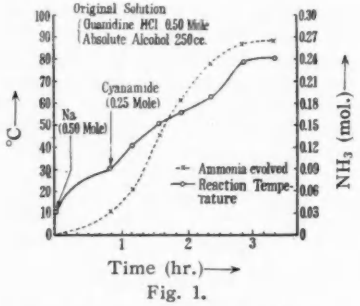


Fig. 1.

After the reaction, the solid (36.50 g.) was filtered off and treated with 100 cc. of water to dissolve sodium chloride only. The residue, washed with water and ethanol, dried, and weighed 7.00 g. (0.063 mole), m.p. 309–312°C, m.p. 316–7°C after crystallization from hot water. A mixture melting point with pure formoguanamine prepared from biguanide[2] showed no depression. Found: N, 62.73. Calcd. for $C_3H_5N_5$: N, 63.04%. The picrate melted at 248°C.

In the mother solution, about 58% of guanidine and 25% of cyanamide were found to remain unchanged together with a trace of biguanide formed[3]. Of course, a part of cyanamide was converted to dicyandiamide.

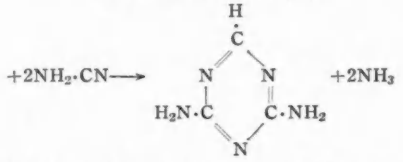
From these results, it was concluded that, in the latter case, guanidine was probably reduced to give an unstable reduced compound (triaminomethane (a part, formamidine $+NH_3$) ?) and it reacted with cyanamide to give formoguanamine according to the following formula.

$NH_2 \cdot C(NH) \cdot NH_2$

$+2H \longrightarrow$ Reduced Compound of guanidine

$(NH_2 \cdot CH(NH_2) \cdot NH_2$ or

$NH_2 \cdot CH{=}NH{+}NH_3$?)



The formation of formoguanamine was an unexpected result and seemed to be very interesting, because the possibility of the reduction of guanidine itself was proved.

Laboratory of Organic Electrochemistry,
Department of Chemical Engineering,
Tokyo Institute of Technology,
Tokyo

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** XLIV, K. Shirai, *J. Chem. Soc. Japan.*, Industrial Chemistry Section, 58, 343 (1955).

1) Under these conditions, cyanamide itself was converted in a considerable yield to dicyandiamide in the presence of guanidine.

2) This sample was prepared by Mr. M. Yamashita according to his procedure (*J. Chem. Soc. Japan*, Industrial Chemistry Section, 54, 786 (1951)) m.p. 318°C.

3) After standing for several months, the authors found a small amount of melamine crystallized out in the mother solution of this experiment.

Sur la Séparation de trois Éléments, l'Étain, l'Antimoine et Tellure, par la Résine échangeuse d'Anion

Par Yukiyoshi SASAKI

(Reçu le 3 Août 1955)

En étudiant le dosage des éléments radioactifs produits par la fission nucléaire, et de l'étain irradié par neutron lent, nous nous sommes proposé de séparer trois métaux, l'étain, l'antimoine et le tellure. Dans ce but nous avons obtenu un bon résultat utilisant la résine échangeuse d'anion fortement basique.

Des essais préliminaires ont montré que ces métaux sont adsorbés sous les formes de chlorocomplexes, $SnCl_6^{2-}$, $SbCl_6^-$ et $TeCl_6^{2-}$ par la résine échangeuse d'anion en solution chlorhydrique concentrée. Lorsque l'acide se dilue, ces complexes commencent à se libérer de la résine se dissociant en cation ou chlorure de non-électrolyte et des anions de chlore.

Pour savoir l'affinité des métaux à la résine, nous avons mesuré des constants d'élution par des expériences chromatographiques utilisant une petite colonne remplie de la résine échangeuse d'anion Dowex 1-x4 fortement basique, sous la forme de chlorure.

Le chlorure du métal en question est mis au sommet de la colonne, et on laisse passer l'acide chlorhydrique pour déplacer le métal le long de la colonne. La courbe d'élution est obtenue par le dosage du liquide émergeante. Le constant d'élution s'exprime par le volume de la résine dans la colonne, divisé par le volume de l'acide chlorhydrique dépensé jusqu'au point de maximum de la courbe d'élution.

Tableau I montre les constants d'élution de ces trois éléments qui sont mesurés en solution chlorhydrique à diverses concentrations. La valeur de 1.3 signifie que le métal n'est pas adsorbé par la résine et passe librement la colonne.

TABLEAU I

CONSTANTS D'ELUTION

Concentration de ClH	0.1	1	2	3	4	6 N
Sn (IV)	1.3	<0.1*	<0.1	<0.1	<0.1	<0.1
Te (IV)		1.3	0.1	<0.1	<0.1	<0.1
Sb (V)		1.3	1.3	1	0.3	<0.1
In (III)	1.3	0.5	—	0.3	—	0.3

* Le constant n'arrive pas à 0.1, mais la valeur précise n'a pas été obtenue.

Tandis que l'adorption et la désorption se réalisent rapidement et complètement pour le tellure et l'indium, l'adsorption irréversible a lieu pour l'antimoine-(V), à savoir, l'acide chlorhydrique à 3N ne peut eluer que 70% de l'antimoine qui était fixé sur la résine, ni l'acide nitrique, ni l'acide perchlorique n'est pas efficase à le désorber.

Etant donné que l'antimoine-(III) se fixe fermement sur la résine, cette adsorption anormale est interprétée en supposant la réduction de l'antimoine-(V) à l'antimoine-(III) dans la résine. Pour éviter la réduction de l'antimoine-(V), la résine à utiliser a été traitée par le brome jusqu'à ce qu'elle fût colorée en jaune*, et de plus, la durée où

l'antimoine serait en contact avec la résine a été minimée autant que possible.

Par ces traitements la quantité de l'antimoine resté dans la résine a été réduite jusqu'à 0.5% de l'antimoine total. L'etain n'est élué que moité par l'acide chlorhydrique à 0.1 N à cause de l'hydrolyse, mais l'acide perchlorique à 2 N le désorbe complètment.

Partant de ces résultats nous avons mis au point la séparation de ces trois métaux utilisant une colonne de verre de 0.85 cm. de diamètre, remplie de la résine Dowex 1-x4 de 50–100 mesh sous la forme de chlorure, traitée par le brome et lavé avec l'acide chlorhydrique à 3 N, jusqu'a une hauteur de 4 cm.

Un mélange à séparer est une solution chlorhydrique à 3 N, 1.5 cm^3 contenant 3 mg. de l'antimoine-(V) 1 mg. du tellure-(IV) 3 mg. de l'étain-(IV) avec les indicateurs radioactifs, ^{113}Sn (112 jours), son derive ^{113m}In (105 minutes), ^{129m}Te (30 jours) et ^{124}Sb (60 jours) de provenance des Etats-Unis. Après avoir laissé adsorber le mélange à étudier en haut de la colonne de la résine, on effectue l'elution avec l'acide chlorhydrique à 3 N pour éluer l'antimoine-(V). L'élution se pursuit pendant 20 cm^3 jusqu'à la disparition de la radioactivité dans le liquide émergeant. Dans ce cas, le constant d'élution a été un peu diminué par l'influence du brome.

Ensuite, l'acide chlorhydrique à 1 N est choisi pour enlever le tellure laissant adsorbé l'étain sur la résine. l'étain est désorbé par l'acide perchlorique à 1.8 N. La solution émergeante est receuillie par fraction de 1 cm^3. Les fractions du tellure et de l'étain sont évaporées à sec sur des assiettes de verre. Etant donné que le chlorure de l'antimoine se volatilise, l'antimoine est précipité et filtré comme sulfure.

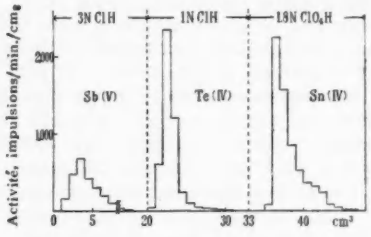

Fig. 1. Courbe d'elution.

Les dosages des métaux dans les fractions ont été réalisés en mesurant leur radioactivité par un conteur de Geiger-Müller après l'quilibre radioactif entre ^{113}Sn et ^{113m}In a été atteint. La Fig. 1 représente la courbe d'elution dans laquelle l'indium élué aux fractions de l'antimoine et du tellure n'existe plus,ma is de la Tableau I il resulte que si l'on désire à séparer l'indium de l'etain, l'acide chlorhydrique à 1–12 N élue l'indium et laisse l'étain sur la résine.

Nous avons repris le même procédé pour traiter les échantillons qui contiennent ces trois métaux dont l'un seul a été marquée avec l'indicateur radioactif.

Ces expériences ont montré que dans le procédé de la séparation donné ci-dessus, la quantité d'un élément qui contamine les fractions des deux autres métaux n'arrive pas à 0.05% de cet élément total.

Laboratoire de Chimie, Faculté de Science
L'Université de Tokio

* La résine échangeuse d'anion adsorbe du brome en solution chlorhydrique concentrée plus strictement qu'en solution peu concentrée. Il est probable que le brome est adsorbé comme Br_2Cl^-.